PRINCIPLES OF CHEMISTRY

HILDEBRAND

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PRINCIPLES OF CHEMISTRY

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PREFACE

This book has grown out of the need for a text-book for the course in General Chemistry and Qualitative Analysis in the University of California. There are, it is true, many excellent texts in existence, but whenever an instructor uses a text written by some one else he faces the dilemma that a departure from the order and manner of presentation of the printed text results in the loss of much of its value to the student, whereas a close adherence to it, on the other hand, interferes with the freedom and individuality, and hence with the enthusiasm and effectiveness of the teacher. Nor can the instructor altogether avoid this dilemma by writing his own book, as probably every one is tempted to do, for the use of any text tends to end the period of experimentation upon the class, and to substitute, therefor, year after year of complacent stereotyped repetition.

Now there are two facts which seem to the writer to indicate a way to avoid these difficulties. The first is that the difficulties of the student are not concerned with the simple matters of fact so much as with general principles, methods and points of view. It is comparatively easy for him to learn the properties and uses of substances from any text-book, lecture or laboratory course, but much harder for him to learn to write equations, to use them in calculations of weight and volume, to understand and apply such principles as the Ionic Theory or the mass law. Repetition, thought and practice are required in such cases.

The second of these facts is that writers of text-books have been in the habit of introducing the general principles in the particular connections which seem best to them at the time of writing, and it is usually unsatisfactory for the instructor to change the order followed by the book. A topic like the mass law, for example, is introduced in a chapter headed Sulfur, and must remain there if the illustrations are to be of any value, whereas, of course, this principle belongs no more under sulfur than it does under any other element, and the instructor using the book may wish to introduce it at some totally different place. On the other hand, the purely descriptive material could be rearranged almost ad libitum.

It seems to the author, accordingly, that the ideal text-book would consist of two volumes, one of general principles, the other of descriptive chemistry. Since, however, the descriptive material is available in so many existing books, the limit of the author's present ambition is a presentation of the principles of chemistry in such a way as to allow, in its use, the maximum flexibility consistent with the subject. It is hoped that the treatment of these principles in this volume is such that the various chapters and sections can be used in connection with almost any arrangement of descriptive material. Furthermore, although a certain logical order has been followed, the effort has been to make the presentation of each topic such that considerable departure from the given order might be possible without loss of intelligibility. Some parts of a chapter such as that on the Periodic System, for example, may well be introduced in a course much earlier than other parts, and the arrangement of paragraph headings throughout has been made with the end in view of facilitating such rearrangement.

This separate treatment of principles, however, is undertaken not only to allow flexibility, but also to emphasize the principles of chemistry to a degree that seems justified by the present status of chemical science. The earlier history of all natural sciences is that of description and classification, and their adepts were necessarily men of well-developed powers of observation and memory rather than of inference and deduction. With the development of the science of chemistry, however, there has arisen a considerable body of general principles which can serve as the basis for deduction, and the profound change in the character of chemical research during the last generation bears witness to the development of the later type of scientist, the one who seeks causes, and aims to develop means for predicting and controlling phenomena. In recognition of this change elementary texts have been "modernized" by the introduction of chapters on the Ionic Theory, Phase Rule, Chemical Equilibrium, etc., but such chapters are often intrusions foreign to the rest of the book, and never become part of the usable tools of the student. Although, of course, chemistry is yet far from being an exact science, we nevertheless have made far more progress in this direction than is recognized in the traditional plan of instruction, and progress in both pure science and industry is becoming constantly more dependent upon ability to predict new facts by the aid of general principles rather than upon a knowledge of existing facts.

A remarkable plea for such a change in the teaching of chemistry is made by the late Professor H. LeChatelier in the preface to his book "Leçons sur Carbone." The entire preface is worth reading by all teachers of chemistry. In

it he says: "Pour comprendre la nécessité de modifier profondément les méthodes d'enseignement de la chimie, il suffit de comparer un cours de chimie et un cours de physique. . . . Dans l'enseignement de la physique on ne parle que des lois des phénomènes naturels. En chimie, au contraire, c'est une énumération indéfinie de petits faits particuliers: Formules de combinaisons, densités, couleurs, action de tel ou tel corps, recettes de preparation, etc. . . . L'enseignement de la chimie minérale est complètement immobile depuis soixante-quinze ans." He goes on to contrast this orthodox method of presentation of chemistry with the chapter headings from the work of Lavoisier: "De la combinaison du calorique. — De la formation des fluides aériformes. — Nomenclature des acides. — Quantité de chaleur dégagée dans les différentes combustions. — De la fermentation putride. — Des sels neutres, etc."

It is not intended, by any means, that this volume should furnish the entire material for a course in general chemistry. While using it as a text for our classes in the form of a preliminary edition, we have provided also a number of copies of standard modern descriptive books on reference shelves readily accessible to the students. Our own course includes much of the traditional descriptive material, and besides, for entrance to the University course, we prescribe High School chemistry, which is usually largely descriptive in nature. Our aim is, however, to develop principles rather than simply to study elements and compounds descriptively. The laboratory manual for our course has been written with this end in view by Professor W. C. Bray and Dr. Ludwig Rosenstein.

It is hoped that the book may prove useful also as reference

for more advanced courses in inorganic chemistry and introductory courses in physical chemistry. For Freshman courses certain parts of the book may be omitted except as a stimulus for students of exceptional ability. Since we shape our courses far too much to meet the needs of the poor student only, such a stimulus is often overlooked.

For whatever merit the book may possess, the author desires to make very great acknowledgments to his colleagues. Our own course has been developed to a large extent in the weekly conferences of instructors, and the freedom of criticism always enjoyed in these meetings has had a very large effect in determining the contents of this volume. Especial thanks are due for the valuable criticism given by Professor G. N. Lewis, Professor W. C. Bray, Dr. W. L. Argo and Dr. G. E. Gibson, who were kind enough to read the manuscript, and to Dr. Wm. Blum, who read the proof.

JOEL H. HILDEBRAND.

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PRINCIPLES OF CHEMISTRY

CHAPTER I

KINDS OF MATTER

The Domain of Chemistry. Various aspects of the material things we see about us may attract our attention, such as the uses to which these things may be put, the beauty of form or color they may possess, or the materials out of which they are made. It is the last of these that is the concern of chemistry. Two vases may have nothing in common from an artistic standpoint, and a vase and a plate may serve entirely different purposes, and yet, from a chemical point of view, all of them may be identical by reason of the material, porcelain, out of which they are made. Chemistry does not concern itself with articles or objects, as typified by such words as chair, pen, bottle, nail, wire, but rather with the substances or materials out of which these and other objects may be made, as typified by such words as wood, glass, iron, copper, clay, sugar. It is one task of the chemist to ascertain all of the qualities or properties of every kind of matter, so that the vast number of different kinds may be recognized and distinguished from each other.

It is also the task of the chemist to determine how these substances or materials may be obtained, or, when obtained, how they may be preserved. The materials out of which

objects are made often do not occur in a free state in Nature. Iron, for example, is found but rarely in the free state, and the enormous quantities of it which are used for making such a multitude of things must be obtained from the various iron ores, by heating them with coke or charcoal in a blast furnace. It is, of course, very important to know how much coke to use with a given amount of ore, and how much iron should be obtained from the ore, because the cost of iron is partly determined by these factors. The chemist, therefore, must be concerned not only with iron, its nature and properties, but also with the conditions necessary for getting it from its ores, and the quantities of the materials involved in the process. And then, finally, he must determine how to prevent loss of iron from rusting.

The housewife, in making biscuits with the aid of baking soda and sour milk, finds that if too little soda is used the biscuits will not be "light," whereas if too much soda is used they will be yellow, and the taste will be impaired. She must therefore know not only that when soda and sour milk are mixed they give a gas that will make the dough porous, but also the relative amounts necessary for the best results.

In the processes just referred to, it is obvious that new kinds of matter have been produced. The iron ore and the coke are quite evidently different stuff from iron. The sour milk loses its sour taste when mixed with sufficient soda, and a gas is evolved quite different from either of the previous materials. Any such change, in which the kind of matter is altered, is called a chemical change, or a **chemical reaction**. When iron is drawn into wire, or made into nails, it is still iron, and no chemical change has taken

place, but when it rusts it is no longer iron but a brown powder of very different nature from iron. When marble is cut into various shapes it is still marble, whether in the form of a statue, a table top or a building block, possessing all of the characteristics by which we recognize it as marble. If, however, we heat it for a while to a high temperature, it changes in appearance, losing weight, becoming the familiar substance we call quicklime. This again is a chemical reaction, since a new substance is produced. Another chemical reaction takes place if we allow water to come in contact with the quicklime. The color changes from light gray to white, heat is evolved, the mass swells and falls apart to a powder, or, if water is in excess, forms a paste. The resulting material is called slaked-lime, a substance with properties different from those of marble or quicklime.

Often we direct our attention, in dealing with chemical reactions, not so much to the nature of the substances involved, or to their relative amounts, as to the energy used up or liberated by the process. When oil burns it unites with something from the air, as we must infer from the necessity of an air supply, and forms gaseous products, which ordinarily do not attract our attention except for the necessity of providing for their escape. The most important thing is the energy made available by the reaction, which we may wish to use for light, heat or power. In a dry cell zinc is used up and electrical energy is obtained. The question as to what becomes of the zinc is overshadowed by the question as to how much electrical energy should be obtained from a definite amount of zinc.

We see, then, that **chemistry is concerned with substances, and their properties; with the changes or reactions whereby**

other substances are formed; with the conditions necessary for bringing about or preventing these reactions; and with the relative amounts of matter and energy involved.

Some hint may be obtained, from the illustrations given above, of the immense importance of chemistry to the material welfare of mankind. Great service has been rendered by those who have applied it to the satisfaction of human needs. It must not be forgotten, however, that these needs are mental and spiritual as well as material, and that to enlarge man's mental horizon is quite as worthy an endeavor as it is to increase his physical comfort. To seek out and discover Nature's mysteries is not a pursuit that requires utilitarian justification. The world owes an incalculable debt to the explorers who have led the way to new fields of thought and endeavor. It is these men who pave the way not only for the miner, the railroad builder and the farmer, but, most important of all, for others who love Nature and whose spirits are enriched by her knowledge. To those having this pioneer spirit chemistry offers wide uncharted realms, to explore which is among the most fascinating of pursuits.

Properties Used to Recognize Substances. Many substances have characteristics so marked that there is little likelihood of their being confused with other substances. The color of copper distinguishes it from other metals. The elasticity of rubber, the taste of sugar, the odor of ether, serve to distinguish these substances, even in the absence of other tests, from those encountered in ordinary life. We constantly apply such obvious tests as those of color, luster, hardness, odor and taste. We distinguish quite readily between solids, liquids and gases. Very often, however, we

need to refine our methods of observation, or to use less obvious properties for distinguishing substances. Instead of being content with saying that lead is "heavier" than iron, we find it desirable to express this "heaviness," or density, numerically by determining the weight of a unit volume, usually the number of grams per cubic centimeter. The refractive index of a transparent body can be determined with great exactness and is a most valuable means of identification. The coefficient of expansion, the conductivity for heat or electricity, the boiling point, the melting point, the heat of fusion or of vaporization, are all quantities which have characteristic values for individual substances, and which may be accurately determined by appropriate methods.

The chemical changes which substances may undergo offer important means of identification. Gold may be indistinguishable in appearance from certain samples of brass, but nitric acid at once differentiates them by dissolving the latter. Powdered talc and starch in a face powder might readily be differentiated by the fact that the latter will swell up and dissolve in boiling water, or that it will readily burn.

Heterogeneous Mixtures. As we attempt to apply our tests to distinguish substances, we notice that some materials give a rather ambiguous answer. What shall we consider to be the color, density or hardness of a piece of granite? On close examination we find it composed of several kinds of minerals, having different degrees of hardness, different colors and different properties in general. Although we might determine the density of a given piece of granite, it would be folly to talk about the density of

granite in general, because the components of granite are present in different proportion in different samples. Granite is obviously a mixture and not a pure substance, and its properties change abruptly from one small region to another. These regions within which the properties suffer no abrupt changes, in this case quartz, mica and feldspar, are called **phases**. A mixture containing more than one phase is called a **heterogeneous mixture**. Another example is muddy water. Here we cannot see the different phases quite so readily, but a microscope or a filter shows quite distinctly that two phases are present. Some alloys, like solder, appear quite uniform to the eye, as if they contained but one phase, whereas, by careful etching with acid and using a microscope with reflected light, it is evident that the alloy is heterogeneous, more than one phase being present.

Evidently, then, the first step in our examination and classification of matter is to separate heterogeneous mixtures into their component homogeneous phases. This may be accomplished by purely mechanical means, which may vary with the nature of the separation. A suspended solid may be removed from a liquid by filtration. A fog (liquid particles) or a smoke (solid particles) may be removed from a gas by the same means. Two solids may be picked apart, though such a process would often be impracticable. Where two kinds of solid particles have different densities it is sometimes possible to employ a liquid whose density is such that one solid will rise to the surface while the other stays on the bottom, as would be the case if a mixture of sand and sawdust were thrown into water. Two liquids which do not mix, like kerosene and water, are easily separated by

skimming or some equivalent process. Where one is emulsified in the other, the highly dispersed globules of the one may often be made to coalesce prior to a separation, as when butter is obtained from cream.

Solutions. Having separated heterogeneous mixtures into single phases, our next step is the examination of these phases. We will find that a phase may consist of one substance, or of two or more substances, when it would be called a **solution**. For example, we may take sugar and water, each a pure substance, and make a solution, uniform throughout in properties. The sugar cannot be seen with a microscope or filtered out by a filter. Such a solution has the same appearance as a pure substance. It can be distinguished from a pure substance, however, by the fact that its properties depend on the relative amounts of the substances from which it is made. The properties of a pure substance are always the same at the same temperature and pressure. Pure water always has the same density, provided that the pressure and temperature at which the density is measured are kept the same. Ice always melts to water at the same temperature unless a different pressure is applied to it, and even then for every pressure there is a definite melting point. Similarly the boiling point of water depends only upon the barometric pressure. The properties of solutions, on the other hand, depend on the composition, as well as on the temperature and pressure. The properties of a sugar solution are not implied when the temperature and pressure are stated, as is the case with pure sugar or pure water. In order to predict the density or sweetness of such a solution, or the temperature at which it would freeze or boil, we would have to know its composi-

tion, *i.e.*, how much sugar there is in a given amount of water. In general, then, **the properties of a solution depend not only upon the temperature and pressure, but upon the composition as well.**

The term "solution" must not be restricted to liquid solutions, although they furnish the most familiar examples. All gases are completely miscible with each other, forming but one phase, so that every mixture of gases is a solution. Alloys of silver and gold, no matter what the relative amounts of the two metals, contain but one kind of crystal, the properties of which, such as density, color, electrical conductivity, melting point, change continuously with the composition. This is a **solid solution**, and may be contrasted with alloys of copper and silver, which contain two kinds of crystals through a certain range of composition. This could be shown, first, by the microscope, second, by the fact that alloys of these latter metals, though of different composition, would all begin to melt at the same temperature. This is true because a change in the proportion of the metals produces no change in the nature of the two crystals but simply in their relative amount, and the melting and boiling points of substances never depend upon how much of the substance is taken.

Hardened steel is a solid solution, for though it contains carbon it shows but one kind of crystal under the microscope, as shown in Fig. 1, just as does wrought iron, Fig. 2, which is nearly pure iron. Gray cast iron, however, contains graphite crystals, as shown in Fig. 3, and is obviously heterogeneous, as is annealed steel, Fig. 4, which consists of an intimate mixture of pure iron, of the kind shown in Fig. 2, with an iron carbide.

Solutions and pure substances can be differentiated experimentally by changing the state of aggregation of part

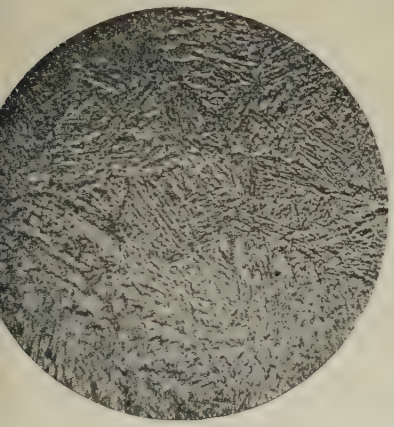


FIG. 1. — Hardened Steel.

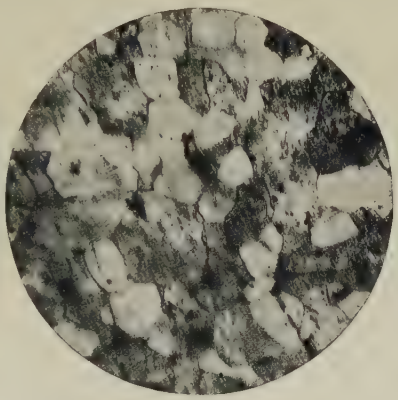


FIG. 2. — Wrought Iron.

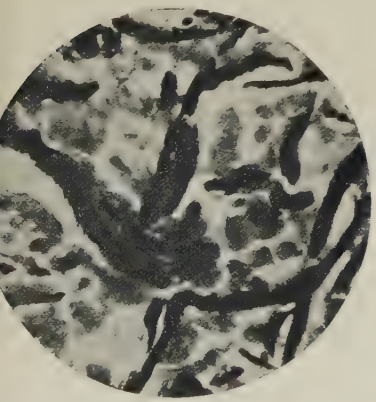


FIG. 3. — Gray Cast Iron.

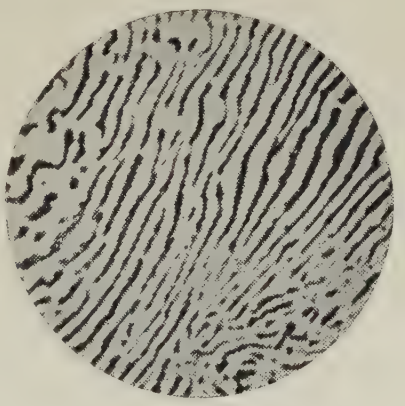


FIG. 4. — Annealed Steel.

of the material, as by melting, crystallizing or boiling, whereupon one component usually changes in state more

readily than the other, so that the new phase will be of different composition from the old and hence have different properties. Air can be shown to be a mixture of gases by liquefying it and allowing the liquid to evaporate slowly. During the process it will be found that the boiling point changes, that the color of the liquid residue changes, and that the air evaporating gradually changes in properties, as shown, for example, by the fact that the brightness with which a candle will burn in it increases gradually from the first to the last portions.

If liquid air is distilled in a scientifically constructed still, it is possible to separate it into two nearly pure constituents, just as water and alcohol can be separated. One of these constituents is found to be slightly lighter than air; it can be condensed to a colorless liquid boiling at $-194°$ C.; it is very inert chemically, reacting with but few other substances. The name **nitrogen** is given to it. The other constituent is slightly heavier than air; it gives, when condensed at low temperatures, a blue liquid boiling at $-182.5°$ C., and it reacts readily with many substances. Ordinary combustible materials burn in it very vigorously. It is called **oxygen.**

Compounds and Elements. Having found out how to distinguish between mixtures and pure substances, let us ask the further question: of what are pure substances made? This question may be answered by means of appropriate chemical reactions. We may determine what substances may be made to unite to form the substance we are investigating, a process called **synthesis**, meaning putting together; or we may separate the substance into simpler constituent substances, a process called **analysis**, meaning

taking apart. If molten lead is exposed to the air, it becomes coated with a scum, and if this scum is constantly removed, the lead entirely changes into another substance, called litharge, with a considerable increase in weight, indicating that something has been absorbed from the air. Of the two main constituents of the air only one, the oxygen, will transform the lead in this way. We would conclude from these facts that the familiar substance litharge is composed of lead and oxygen, or, as chemists would say, is a **compound** of lead and oxygen. This would be the synthesis of litharge.

On the other hand, we might take some litharge, put it into a crucible, heat it to a red heat, pass over it some illuminating gas, and we would find that it changed into lead, with a loss in weight. Evidently litharge contains lead plus some other constituent which has been removed by the illuminating gas. Further experiments might be performed to prove this other constituent to be oxygen. This would be the analysis of litharge, and from it, likewise, we would conclude that litharge is a compound of lead and oxygen.

Again, if we pass an electric current through water, using platinum or gold electrodes to introduce the current into the water, we find that gases are given off at the electrodes and that water is used up. If we collect the gas given off at the negative electrode, we find that it is very light, that soap bubbles filled with it rise like balloons, and that it will burn in air with a faintly luminous, very hot flame. To this gas is given the name **hydrogen**. The other gas is slightly heavier than air, and will not burn in air, but burning substances thrust into it will continue to burn with greatly increased vigor and brilliancy. This gas we may

identify as oxygen, which we have found to be also one of the constituents of air. From this analysis of water we would conclude that water is a compound of hydrogen and oxygen. The analysis might be made in many other ways. We might also synthesize water by allowing hydrogen and oxygen to combine, which they do very readily.

Now it has never been possible to resolve lead, oxygen and hydrogen into simpler substances. These substances, and all others which have never by ordinary chemical reactions * been resolved into simpler substances, are called **elements**. There are known at the present time about eighty-three elements. They can form almost endless combinations with each other; considerably over one hundred thousand are known and new ones are constantly being prepared.

The accompanying table contains a list of the chemical elements. Many of them are well-known substances. Many are rare, occurring in but small quantities.

Symbols. Along with each element in the table is given a characteristic number, whose significance will be explained later, and also a symbol used to designate the element. It consists of the initial letter of the name, followed, where necessary to distinguish between several elements having the same initial, by a second appropriate letter. In many cases the symbol follows the Latin name of the element rather than the English name, allowing the symbols to be practically the same in all the principal languages. Thus, the symbol for iron is Fe, from the Latin *ferrum;* that for gold is Au, from the Latin *aurum*, etc.

* Certain elements decompose into others by a different type of change called radioactive, to be treated in Chapter XVI.

THE CHEMICAL ELEMENTS

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Beryllium*	Be	9.1	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Caesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.005	Praseodymium	Pr	140.9
Cerium	Ce	140.25	Radium	Ra	226.0
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulfur	S	32.06
Germanium	Ge	72.5	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

* Also called Glucinum, symbol Gl.

Classification of the Elements. The elements may be classified in various ways, all of which might be useful for certain purposes. Some of them are solids, some liquids, and some gases, at ordinary temperature and pressure. This is, however, not a very fundamental distinction, as each element may be made to exist in any of these states by suitable alterations in temperature and pressure. A most useful classification is that furnished by the Periodic System, whereby the elements are arranged in families or groups which show similar properties. This arrangement will be used very extensively later, after we have explained the basis upon which it is made. One of the most significant of all divisions is that into metals and non-metals. The general characteristics of metals and non-metals are familiar to all. Metals are characterized by an appearance called metallic luster, by malleability and ductility, and by relatively high conductivity for heat and electricity. These physical differences are accompanied by fundamental differences in chemical behavior to be discussed later.

From what has just been said it must not be supposed that the metallic state is peculiar to elements. There are many compounds which are metallic also. The further classification of compounds will, however, be deferred to a later chapter, where we will see that the metallic or non-metallic character of the component elements furnishes the basis for this classification.

It must not be thought that all elements fall readily into these two classes. In fact the two classes shade into each other, as illustrated by carbon, which in the form of graphite has some metallic luster and is a fair conductor of electricity, or by arsenic, which has metallic luster but is very brittle.

Most of our schemes of classification are arbitrary, for our own convenience, and are not due to sharp natural boundaries.

Summary. The classification of materials that has been presented in this chapter may be summarized in the following table. It is not important to memorize the table, but it is important to understand the nature of the distinctions it indicates.

Kinds of Matter.

Heterogeneous.	**Homogeneous.**
Consisting of more than one phase.	Consisting of one phase.

Pure Substances.	**Solutions.**
Constant Composition.	Variable Composition.

Compounds.	**Elements.**

Metals.	**Non-metals.**

EXERCISES

1. What is the distinction between the terms "object" and "substance"?

2. Name a number of properties which serve to identify and distinguish substances.

3. How could you distinguish between nickel and silver? Gold and brass? Alcohol and water? Glass and rock crystal (quartz)? Starch and talc powder? Salt and baking soda? Solid and plated silverware? Glass and diamond? Ether and chloroform?

4. Classify the following materials according to the above table, giving reasons; where you are not sure of the classification devise an experiment which would enable you to decide: milk, bronze, illuminating gas, glass, wheat flour, a five-cent piece, well-water, gasoline, cast iron, plaster of Paris, white lead, sugar, gold, sulfur.

5. Define, or at least use correctly in a sentence, each of the following terms: phase, element, symbol, metal, substance, solution, property, compound, density, heat of fusion.

CHAPTER II

THE GAS LAWS AND THE KINETIC THEORY

While we are discussing the general properties of substances it will be profitable to consider certain properties of gases, on account of the existence of important uniformities in their behavior. When solids and liquids are heated, in nearly all instances they expand, but the rate of expansion with the temperature is a specific property of each substance. The same holds true for the compressibility of solids and liquids. However, when we investigate the behavior of gases with respect to alterations in temperature and pressure, we find that the effect on the volume is almost the same no matter what gas is being examined. One does not need to know the name of the gas in order to predict how its volume will change under the influence of changing pressure or temperature. In making such predictions we may have in mind either certain formulas which express the results of experiments upon gases, or else a theory as to the nature of gases which enables us to predict the behavior actually found by experiment. This twofold approach to scientific truth has been quite general, sometimes experiment leading to the discovery of new laws to be afterward explained by a theory, sometimes theory suggesting laws whose truth must be tested experimentally. In the present instance there are advantages in approaching the problem from the theoretical standpoint, since the theory is so simple and leads so obviously to the correct mathematics, making

it unnecessary to commit to memory formulas almost sure to be forgotten or misapplied.

Kinetic Theory. The fundamental difference between gases on the one hand, and liquids and solids on the other, is the **tendency of gases to expand indefinitely**, so as to fill completely any vessel in which they are contained. If a quantity of gas is introduced into an evacuated vessel, it distributes itself almost instantly throughout the whole space at its disposal, showing a tendency to still further expansion by exerting a pressure on all parts of the walls of the vessel.

If the vessel already contains one gas, and another gas is admitted, it will be found after allowing sufficient time to elapse, that both gases are equally distributed throughout the vessel. For example, if ammonia is exposed to the air in one part of a room in which the air is perfectly still, a person in a different part of the room will soon be able to smell the ammonia. This process, whereby one substance works its way through another, is called **diffusion.**

Now, let us ask the question, what sort of structure must a gas possess in order to account for these phenomena? The most satisfactory picture is that furnished by the **kinetic theory**, which assumes that a gas is composed of particles called **molecules**, whose size is very small compared with the distance between them, and that each molecule is in rapid motion, colliding with other molecules and with the walls of the containing vessel.* It is these im-

* An idea of the actual values calculated may be obtained from the following figures for oxygen. At one atmosphere pressure and 0° C., one cubic centimeter of oxygen contains 28×10^{18} molecules, moving with an average velocity of 0.66 kilometer per second (about $\frac{1}{4}$ mile per second). Each molecule travels on an average about 1000 times its own diameter before colliding with another molecule.

pacts which produce the observed pressure, a series of rapid impacts obviously having the effect of a steady pressure. The further assumption is made that the average velocity of the molecules, and hence the pressure produced upon the walls of the vessel, depends upon the temperature, increasing as the latter increases. The molecules are in such rapid motion, and are most of the time so far apart, relatively, that their mutual attractions have very little effect.

This picture of the condition of gases has proved to be of such immense service in explaining and predicting their properties that it is hardly questioned by scientists at the present time.

Relation between Quantity and Pressure When Volume and Temperature Are Constant. Let us see first, how, on the basis of the theory just given, we should expect changes in the amount of a gas to be related numerically to changes in pressure. Imagine a gas inclosed in a vessel provided with a cock, as represented in Fig. 5, *a*. The vessel is supposed to be immersed in a bath to preserve constant temperature. Let us have a very few molecules in the vessel, and visualize them by the dots in the figure. These molecules will all be in rapid rectilinear motion, some moving faster, some more slowly, between impacts, but with a certain average velocity depending on the temperature, producing a definite pressure on the vessel walls as they rebound from them. Suppose, now, we introduce an equal number of the same kind of molecules through the valve, producing the condition illustrated in Fig. 5, *b*. It is obvious that since the volume of the vessel remains the same, and the average speed of the molecules is kept the same by the action of the bath in maintaining constant temperature, the only

effect of the doubling of the amount of gas is merely to double the number of impacts in a given time per unit of area of the vessel walls, and hence to double the pressure. Evidently we would expect any change in the number of molecules in the vessel to produce a proportional change in the pressure, and since the number of molecules depends

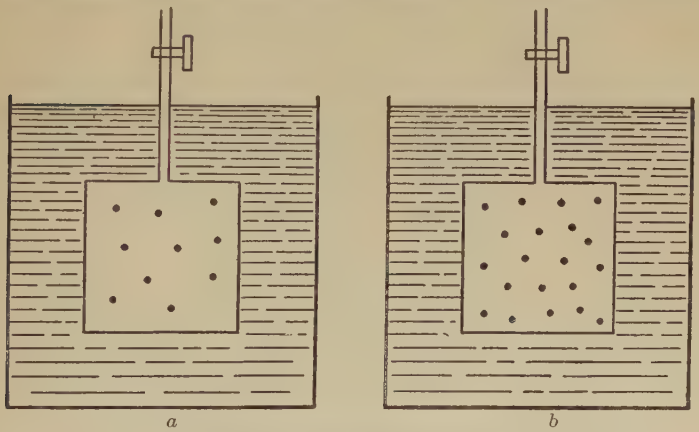


FIG. 5. — Relation between Quantity and Pressure of a Gas.

on the amount of the gas, we can make the general deduction that **when temperature and volume are kept constant the pressure of a gas is proportional to the amount present.**

As an example of how this may be applied let us consider a tank, with an attached pressure gauge, containing any gas. Allow the gas to escape until the pressure falls from 100 lb. per square inch to 30 lb. It is evident, since the pressure has fallen to 0.3 of its initial value, that there remains in the tank only 0.3 of the gas originally present.

Relation between Pressure and Volume When Temperature and Amount Are Constant. Let us imagine, next, that

the gas is contained in a cylinder like that of a steam engine, with a movable piston, as in Fig. 6, so that the volume of the inclosed gas may be altered without changing the amount. If, now, the piston is pushed down from the position represented by *a*, in the figure, to that represented by *b*,

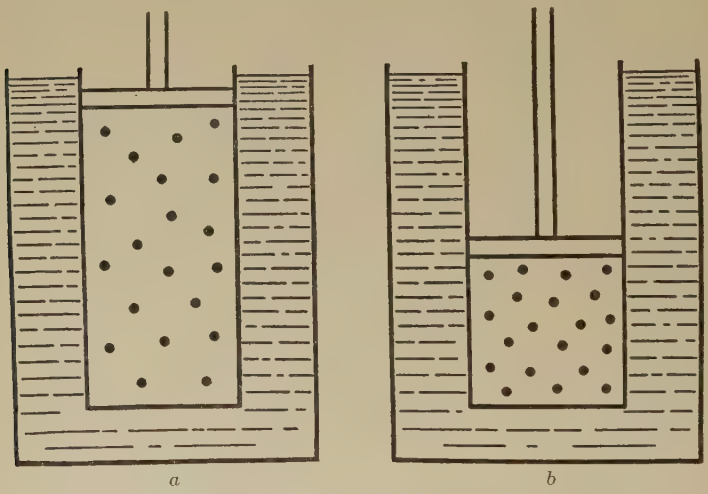


FIG. 6. — Relation between Pressure and Volume of a Gas.

where the volume is half as great, the number of impacts on a given area of the walls in a given time will be doubled. While the piston is being pushed down, the molecules striking it will rebound a little faster than before, causing a slight increase in temperature,* so that we must wait a moment till this temperature has been lowered to that of the bath surrounding the cylinder, when the average speed of the molecules will be the same as before the piston was

* This effect may be noticed in the heating of the pump when a bicycle or automobile tire is pumped up.

pushed down. Since the number of impacts on a given area of the walls has been doubled, the pressure is likewise twice what it was before the piston was moved. Evidently, if the volume were made one third as great as at first, the pressure would become three times as great, etc., so that we may conclude in general that **when the temperature and amount of gas are constant the pressure is inversely proportional to the volume.** This is usually called Boyle's Law.

As an example, let us calculate the final volume when 10 liters of gas at a pressure of 76 cm. of mercury is subjected to a pressure of 19 cm. Since the pressure is **decreased** in the ratio nineteen seventy-sixths, the volume will be **increased** in the same ratio, becoming seventy-six nineteenths of 10 liters, the original volume, or 40 liters.

Relation between Pressure and Concentration When Temperature Is Constant. The ratio between the amount of material and the volume in which it is contained, or the amount in unit volume, is called its **concentration.** Evidently it is the concentration which determines the number of impacts, and hence the pressure, so long as the speed of the molecules is unaltered. If, for example, 2 g. of a certain gas in 5 liters exerted a pressure of 2 atmospheres, then 1 g. of the same gas at the same temperature in a volume of 10 liters would be only one fourth as concentrated, and would exert only one fourth of the pressure, which would be one half atmosphere. In general, we may say that **the pressure of a gas is proportional to its concentration when the temperature is constant.**

Relation between the Pressure, Mass and Speed of the Molecules. Although, as has been said, the pressure exerted

by a gas depends upon the velocity of its molecules, it is not directly proportional to the speed, for if the speed is doubled, not only does each molecule hit the vessel walls twice as often, but also twice as hard, for the momentum of each molecule is doubled by doubling the speed. The pressure is thus proportional to the square of the average velocity of the molecules, and hence is proportional to their mean kinetic energy. Moreover, the momentum of each impact is proportional to the mass of the molecules. A heavy molecule would exert more pressure than would a light one moving at the same speed. In a mixture of gases the different kinds of molecules must all have the same kinetic energy, hence light molecules, like those of hydrogen, must move much faster than heavier ones, like those of oxygen.

Effect of Temperature, when Amount is Constant. Let us next see how a gas would be affected by a change in the temperature. It will be simplest, first, to consider the effect of this change upon the pressure and volume separately, keeping one constant while the other is allowed to vary. We will imagine a constant weight on the piston of the cylinder containing the gas, so that the volume may vary while the pressure remains the same. We may now vary the temperature by altering that of the bath in which the cylinder is immersed. If the tempera-

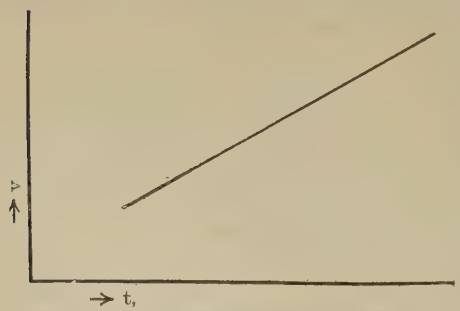


FIG. 7. — Relation between Temperature and Volume of a Gas.

ture of the gas is increased, we would expect, in terms of our theory, that the molecules would gain in kinetic energy, moving faster and hitting the vessel walls and the piston both harder and more frequently, forcing the latter upwards until the reduction in the number of impacts in a given time compensates for the greater force of each impact. It is found by experiment that this increase in volume is uniform, as expressed by the plot in Fig. 7.

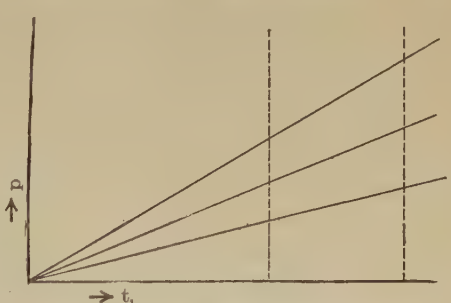


FIG. 8. — Relation between Temperature and Pressure of a Gas.

Absolute Zero of Temperature. Similarly, if the piston is not permitted to move, so that the volume remains constant, an increase in temperature would be expected to increase the kinetic energy of the molecules, resulting in harder and more frequent impacts, and hence an increase in pressure. It is found that the increase in pressure with temperature is uniform, as expressed by the plot in Fig. 8, similar to the previous case. By careful measurements the increase is found to amount to $\frac{1}{273}$ of the value of the pressure at 0° C. We are led naturally to inquire the effect of a continued **decrease** in temperature. Diminishing the pressure $\frac{1}{273}$ of its value at 0° C. for every degree the temperature is lowered, would give no pressure at all at − 273° C. (more exactly, − 273.09° C.).

What does this mean in terms of the kinetic theory? Since we have attributed gas pressure to the impacts of

gas molecules moving with an energy depending on the temperature, when the pressure becomes zero we must conclude that the molecules are no longer in motion, and that we have reached the **Absolute Zero** of temperature. A lower temperature is inconceivable in terms of our theory. This remarkable conclusion is confirmed by the behavior of other properties, many of which approach either zero or infinity, as the temperature approaches – 273° C.

It is both logical, therefore, and for many scientific purposes more convenient, to reckon temperature from the absolute zero, which is 273° below the centigrade zero. We denote absolute temperature by A. On this scale the melting point of ice, 0° C., is + 273° A.; 17° C. is 273 + 17, or 290° A, and in general, letting T and t stand for temperature on the absolute and centigrade scales respectively,

$$T = t + 273.$$

The most convenient way of expressing the effect of temperature on the pressure is to say that **when the amount and volume of a gas are kept constant, the pressure is proportional to the absolute temperature**, since both depend upon the kinetic energy of the molecules.

As an example, let us find the final pressure produced when a tank of gas under a pressure of 10 atmospheres is cooled from 40° C. to 18° C. 40° C. is 313° A., and 18° C. is 291° A. Since the absolute temperature has been lowered to $\frac{291}{313}$ of its initial value, the kinetic energy of the molecules will be lowered to $\frac{291}{313}$ of its initial value, and hence the pressure will be lowered to the same fraction of its initial value, which is $\frac{291}{313}$ of 10 atmospheres, or 9.3 atmospheres.

When the amount of gas and the pressure are kept constant, any change in the absolute temperature, with its proportionate change in the kinetic energy of the molecules, must be compensated by a proportionate change in volume.

Suppose, for example, that we have 250 cc. of gas at 27° C., and wish to determine at what temperature the volume will become 200 cc The new volume will be $\frac{200}{250}$, or 0.8 of the old volume, hence the **absolute** temperature will be reduced to 0.8 of its initial value, or from 300° A. to 240° A., which is − 33° C.

Effect of Changing Both Temperature and Pressure, when Amount of Gas is Constant. When any two of the factors pressure, temperature and volume are changed, the effect on the third can be calculated by separating the process into two steps similar to the above. For example, suppose we have 50.0 cc. of gas at 74 cm. pressure and 20° C., and wish to know the volume it would occupy under **standard conditions**, which are **1 atmosphere (76 cm. of mercury) and 0° C.** If we first change the pressure to the final value, since the pressure is increased, the volume will be diminished to $\frac{74}{76}$ of 50.0 cc. Next, keeping the pressure constant, let us change the temperature from 20° C., which is 293° A., to 0° C., or 273° A. This will cause a further diminution in volume in the ratio $\frac{273}{293}$, so that the result of both changes is $\frac{273}{293} \times \frac{74}{76} \times 50.0$ cc., or 45.3 cc.

The several gas laws which we have just deduced from the kinetic theory, and which are found to be in accord with experiment, may be expressed by algebraic equations, and may be combined into one fundamental general equation. When one has to apply the gas laws frequently, it is wise

to use equations, as the mathematical expression of a law makes it easier to use. As has been said, "mathematics is a substitute for thought"; it enables one to represent briefly the result of thought, so that the process may be repeated in the future without repeating the reasoning. When, however, the formula is used without the previous thought process, as when it is copied out of a textbook, there is the danger that it will be misapplied or forgotten, and even when applied correctly the process is nearly devoid of educational value. Instead of depending on the memory to retain several algebraic equations, we may use the kinetic theory, a very simple conception, and by the aid of easy logic solve any problem in the gas laws, as illustrated above. The only numerical value that needs to be remembered is that 0° C. is 273° A.

In drawing the various conclusions given above concerning the relations between pressure, volume, amount and temperature, we must remember that we have assumed that when the gases are sufficiently expanded the volume occupied by the molecules themselves is negligible compared with the volume of the vessel, also that they are so far apart and moving with such high velocity that their mutual attractions can be neglected. The higher the temperature and the lower the concentration, the more nearly do these assumptions correspond to the truth. On the other hand, as the temperature is lowered and as the concentration is increased, increasing deviations are to be expected from the behavior previously deduced, becoming more and more marked until the attractive forces become sufficient to cause the molecules to condense to the liquid state. The conditions under which this condensation takes place ob-

viously depend upon the kind of molecules involved. With the gas helium, at a pressure of one atmosphere, the temperature must be lowered to 4.5° A. before liquefaction takes place.

Partial Pressure of Different Gases in Mixtures. The kinetic theory also enables us to predict correctly certain properties of gaseous mixtures. In the first place, we would expect the gas laws to hold for mixtures of gases as well as for pure gases, as is indeed the case. In the second place, we would expect the molecules of one species to maintain the same average kinetic energy at the same temperature regardless of the presence of any other species of molecules, and therefore the part of the pressure which is due to the impacts on the vessel walls of one species, called the partial pressure of that gas, would be the same no matter what other gases are present. This may be expressed by saying that **the total pressure in a mixture of gases equals the sum of the partial pressures**. This law is usually known as Dalton's Law. By way of illustration, let us suppose a closed vessel containing water and carbon dioxide gas maintained at a constant temperature. Some of the carbon dioxide will dissolve in the water. Suppose now that some other gas, say nitrogen, is injected into the same vessel. How would this affect the amount of carbon dioxide dissolved in the water? Without the aid of the kinetic theory one might suppose that more carbon dioxide would be forced into the water, but from the molecular-kinetic standpoint we see that the number and momentum of the carbon dioxide molecules striking the water surface, upon which alone the solubility of the gas depends, are practically unaltered by the presence of the nitrogen molecules.

Again, suppose we consider two vessels of equal size, one evacuated and the other containing oxygen, both kept at the same temperature. If water is introduced into the first one, a little of it will vaporize, since the molecules of the liquid are in rapid motion with a velocity depending on the temperature, and certain molecules at the surface which have unusually high velocities may be able to escape the attraction of the liquid and go into the vapor phase. As the number of molecules in the vapor phase increases, there is a constantly increasing chance that some of them, moving more slowly than usual, will be caught into the liquid again, instead of rebounding at the surface. The concentration of molecules in the vapor state thus tends to become adjusted, so that there is an equilibrium or balance between the two phases such that the number of molecules of liquid vaporizing in a given time just equals the number of molecules of water condensing in the same time. The pressure of vapor necessary for this equilibrium depends on the nature of the liquid and on the temperature, increasing as indicated by the curve in Fig. 9. It is obvious that this pressure will not depend on the extent of the liquid surface, as an increase in surface has the same effect on the number of molecules vaporizing as it has on the number condensing, so that the net effect is zero.

Suppose, now, we admit water to the second vessel, containing oxygen. Evidently the tendency of molecules of liquid to escape will be the same as before, but the vaporized molecules will be unable to distribute themselves so rapidly throughout the vessel, since they must diffuse through oxygen molecules which collide with them and retard their progress. Hence the liquid will evaporate more slowly than in the

previous case, where oxygen was absent, but eventually the molecules of water vapor will be distributed throughout the vessel just as if the oxygen were absent, and the partial

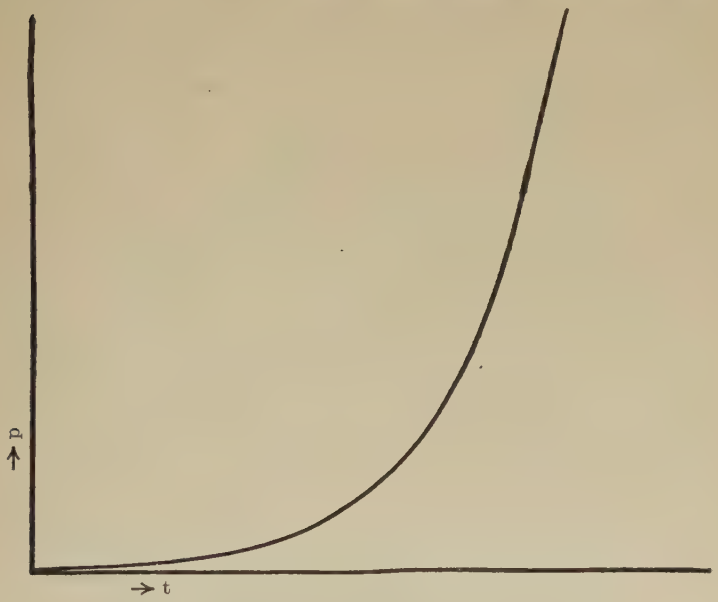


FIG. 9. — Typical Vapor Pressure Curve of a Liquid.

pressure of the water vapor will be independent of the other gas (or gases) present.

Relation between the Pressure of a Gas and Its Solubility in a Liquid. When a gas is placed over the surface of a liquid, it dissolves to an extent dependent on the nature of the gas, the nature of the liquid, the temperature and the pressure of the gas. When no more gas will dissolve in the liquid, we have a state of equilibrium, in which the number of molecules of gas being caught

into the liquid in a given time is the same as the number escaping.

Suppose, now, that more of the same gas is introduced into the space above the liquid. If the temperature is kept the same, the momentum of the molecules striking the surface of the liquid is unaltered, but the number so striking is increased, so that more of them enter the liquid than escape from it, until the added number of dissolved molecules finally increases the number escaping until it again equals the number entering. An increase, therefore, in the pressure of the gas above the liquid causes an increase in the amount of gas dissolved by it. We would naturally expect this amount dissolved to be proportional to the pressure, which is approximately true for gases which are not too soluble. This is known as **Henry's Law.**

Avogadro's Rule. One more consequence of the kinetic theory should be given at this time, as it will play a very important part in the reasoning in Chapter III.

When two different gases are at the same temperature, the average kinetic energy of the two different kinds of molecules is the same. We conclude that this is true from the fact that when two different gases at the same temperature are mixed the total resulting pressure is the sum of the partial pressures each gas would have if the other were absent, hence the kinetic energy of neither is altered by the mixing, which can be the case only when they have the same kinetic energy before mixing. Let us then take, in two vessels of equal volume, such amounts of two different gases at the same temperature that their pressures will be the same. Now we have seen that the pressure of a gas depends upon the number of molecules, their kinetic energy

and the volume they occupy, and upon no other factors. Since, therefore, we have chosen equal pressures, volumes and temperatures (and hence kinetic energies) the only other factor, the number of molecules in the two quantities of gas, must likewise be the same. In other words, equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules. This was first announced by an Italian physicist, Avogadro, in 1811, and is usually called **Avogadro's Rule** or Hypothesis. We will use it presently to measure the relative numbers of molecules involved in chemical reactions.

EXERCISES

1. Does the height of the mercury column of a barometer depend on the cross-section? Explain.

2. If a tank contains gas at a pressure of 100 lb. per square inch, and gas is allowed to escape till the pressure becomes 40 lb. per square inch, the temperature being kept the same, what proportion of the original amount of gas remains in the tank?

3. A quantity of gas having a volume of 150 cc. and a pressure of 800 mm. is expanded, the temperature being kept the same, to a volume of 750 cc. What is the final pressure?

Ans. 160 mm.

4. What volume of oxygen, measured at 20° and 1 atmos. would be required to fill a 10-liter tank, at the same temperature, to a pressure of 25 atmos.? *Ans.* 250 liters.

5. A flask is heated to a temperature of 100° while open to the air, the barometric pressure being 755 mm. It is then closed and allowed to cool at 27°. What is the final pressure?

Ans. 607 mm.

6. A quantity of gas has a volume of 60 cc. at 27° C. At what temperature will its volume become 50 cc.? *Ans.* − 23° C.

7. A quantity of hydrogen measured 24.8 cc. at 18° C. and 765 mm. What volume would it occupy under standard conditions? (1 atmos. and 0° C.) *Ans.* 23.4 cc.

8. 1 liter of carbon dioxide weighs 1.96 g. under standard conditions. What weight of the gas is contained at 18° C., in a tank having a capacity of 20 liters, the pressure being 5 atmos.?

Ans. 184 g.

9. If a 2-liter vessel containing oxygen at a pressure of 1 atmos. is connected with a 5-liter vessel containing nitrogen at a pressure of 4 atmos., what will be the partial pressure of each gas after diffusion has taken place? What will be the total pressure?

Ans. Oxygen, 0.286 atmos.; nitrogen, 2.857 atmos.; total, 3.143 atmos.

10. If a 5-liter vessel contains 12 g. of a gas at 2 atmospheres pressure, what will be the concentration if more of the same gas is pumped in till the pressure becomes 3 atmos., the temperature remaining the same? *Ans.* 3.6 g. per liter.

11. Formulas may be derived for the gas laws by carrying out the reasoning as given, for example, on p. 25, but using the general symbols instead of numbers. Derive the relation between pressure, volume and temperature in this way using p, v and T for the initial values, respectively, and p', v' and T' for the final values. Derive a similar relation between the pressure, temperature and amount of gas (w) when the volume is constant.

12. If 2 g. of a certain gas dissolves in 1 liter of water, at 15° and 1 atmos. pressure, what amount of it would you expect to dissolve in 12 liters of water at 15° under a pressure of 0.3 atmos.?

Ans. 7.2 g.

13. If 1 liter of water dissolves 1 liter of a certain gas at 1 atmos. pressure, what volume of the gas, measured at 5 atmos., would dissolve under the latter pressure in 1 liter of water at the same temperature? *Ans.* 1 liter.

CHAPTER III

WEIGHT RELATIONS IN CHEMICAL REACTIONS. ATOMIC THEORY

An examination of the amounts of material involved is fundamental to an understanding of the chemical reactions. The practical importance of this has been referred to already in Chapter I, but we shall soon see that further consideration of these relations gives rise to theories and laws which lie at the very foundation of the structure of modern chemical science.

Law of the Conservation of Mass. Everyday experience teaches us that many changes in matter take place without any change in weight of the materials involved (weight being the usual measure of mass). Thus 100 lb. of ice, on melting, give 100 lb. of water; 1 lb. of salt dissolved in 10 lb. of water gives 11 lb. of solution; the weight of slaked lime equals the weight of quicklime from which it is made plus the weight of the water added in slaking. It is true that there is a loss in weight when quicklime is made from limestone, but that is because a gas, carbon dioxide, is given off, and if this were caught, compressed into a cylinder, as is often done, and weighed, its weight would be found exactly equal to the loss in weight when the limestone changed into quicklime. Similarly, when something burns, it may seem to disappear, but that is only because gases are formed which may escape notice. If a candle is allowed to burn in a closed vessel, no change in weight can be detected.

As a result of vast scientific experience it may be asserted with great confidence that in every chemical reaction the sum of the masses of the products is the same as that of the substances taken. This is known as the **Law of the Conservation of Mass**, or sometimes as the **Indestructibility of Matter**. It has been tested with considerable accuracy in millions of cases, and with extreme accuracy in a number of them, so that there is hardly another scientific law in which we have such confidence.

Law of Simple Multiple Proportions.* When pure substances are analyzed there is frequently found more than one compound of the same elements, the difference being due to the different proportions in which the elements are united. For example, there are three oxides of lead: litharge, used in glazing pottery, red lead, used in certain paints, and lead dioxide, which gives the brown color to the heads of certain kinds of matches, and which forms the positive plate of a lead storage battery. The proportion of lead to oxygen in these three compounds is found by analysis to be as follows:

Litharge, 1 part lead to 0.0772 part oxygen.

Red Lead, 1 part lead to 0.1029 ($= \frac{4}{3} \times 0.0772$) part oxygen.

Lead Dioxide, 1 part lead to 0.1544 ($= 2 \times 0.0772$) part oxygen.

* It is customary to consider a "Law of Definite Proportions," but since the identification of the pure substances, to which alone it can be applied, involves constancy of composition, as explained in Chapter I, it should be evident that this "law" is simply the definition of a pure substance, reversed. Experiments to prove this law to the student are always carefully selected so as to avoid solutions, without, however, explaining why such selection is necessary. An adequate definition of chemical compounds, including their differentiation from solutions, makes the law of definite proportions a superfluity.

It is very striking that the proportions of oxygen in the red lead and lead dioxide are simple multiples of that in litharge, $\frac{4}{3}$ and 2, respectively.

Again, in addition to water, we know of another compound of hydrogen and oxygen, hydrogen peroxide, a solution of which in water is found in almost every medicine closet for use as an antiseptic, cleansing or bleaching agent. This substance is unstable, and readily gives up half of the oxygen it contains, leaving water. The relative amounts of hydrogen and oxygen in water and in hydrogen peroxide are as follows:

Water, 1 part hydrogen to 7.94 parts oxygen.
Hydrogen Peroxide, 1 part hydrogen to 15.88 parts oxygen.

In proportion to the hydrogen there is just twice as much oxygen in the second compound as in the first. An almost endless number of illustrations of this nature might be given, and we would find that whenever the same elements form more than one compound, if the weights are in the ratio a to b in one they will be in some simple multiple of this in another, such as a to 2 b, a to 3 b, 2 a to 3 b, 3 a to 4 b. The same simplicity is apparent when more than two elements combine to form different compounds. This experience is summarized in the **Law of Simple Multiple Proportions**, which may be stated as follows: whenever the same elements form more than one compound, their proportions in the different compounds are simple multiples of each other.

The Atomic Theory. The existence of the law of simple multiple proportions suggests the question, what fundamental quality of matter is responsible for this behavior?

Why is the proportion of an element in a second compound always twice, three times, etc., what it is in the first, never, for example, 1.376 times what it is in the first? This state of affairs could presumably be true only if each chemical element were composed of minute particles, which we call **atoms**, all alike for the same element. Compounds are formed by simple combinations of different kinds of atoms. For example, one atom of element A, having weight a, might combine with one atom of element B, having a weight b, to form a particle of a compound AB. It is obvious that no matter how many of these particles we take, the ratio of the weights of the elements in the compound would be a to b. The same elements might also form a different compound by a different combination of atoms, such as by one atom of A combining with two atoms of B, to form a particle which may be designated by AB_2. Evidently the ratio of weights of the elements A and B in a particle of this compound, and hence in any number of particles, would be a to $2\,b$. There is here twice as much of element B with respect to A in the second compound, AB_2, as in the first, AB, in accordance with the experience summarized in the law of simple multiple proportions. If still other compounds of A and B are formed, we would expect other simple combinations of atoms, like A_2B, AB_3, A_2B_3, A_3B_2, etc. Accordingly, if the ratio of the weights of A and B in one compound is a/b, we would expect to find in another compound some such ratio as $2\,a/b$, $a/3\,b$, $2\,a/3\,b$, $3\,a/2\,b$.

There are two ways in which we may imagine matter to be constituted, either it is continuous, as it appears to the eye, so that we might go on subdividing it indefinitely and never reach any portion, however small, that could not be

still further subdivided without losing its identity, or else matter may have a granular structure, so that when we have subdivided it until these ultimate grains are reached, no further subdivision is possible without fundamentally altering the nature of the material. That the latter assumption corresponds to the facts is strongly indicated by the success of the kinetic theory in explaining the physical properties of gases, and now we find that a study of chemical changes points to the same conclusion. If we add to this the evidence furnished by radioactive phenomena and colloids, to be discussed in later chapters, we may well feel that the atomic structure of matter is more than a mere theory, and rather an established fact. We owe this atomic theory of matter chiefly to the English schoolmaster-chemist, John Dalton.

Atoms and Molecules. Formulas. We may now consider a little more closely the molecules implied by the kinetic theory and regard them as little groups of atoms, whose kind, number and arrangement in the molecule determine the nature of the substance. Thus water, which we can easily prove to be composed of the elements hydrogen and oxygen in the approximate weight ratio 1 to 8, consists of molecules, each composed of atoms of hydrogen and oxygen. We will now extend the meaning of the symbols H and O to signify not only the elements hydrogen and oxygen respectively, as in Chapter I, but also one atom of each element. We cannot be sure, without the aid of the subject treated in Chapter IV, just how many atoms of each kind there are in a molecule of water, and we may make several assumptions. There may be one atom of each element in a molecule of water, indicated by the combination of the **symbols** of the elements H and O into the **formula**

of the molecule of the compound, HO. If this represents the molecule of water, then we must represent that of hydrogen peroxide, which contains twice as much oxygen in proportion to the hydrogen, by the formula HO_2, and the atom of oxygen must weigh 8 times as much as the atom of hydrogen. Again, the formula of water may be H_2O, indicating two atoms of hydrogen and one of oxygen in the molecule, in which case the molecule of hydrogen peroxide would have to be HO, or H_2O_2, etc., the atom of oxygen being 16 times as heavy as that of hydrogen, in order to account for the observed composition of these two substances. Still other simple assumptions with corresponding relative atomic weights might be made. As set forth in the following chapter, we have satisfactory evidence that the second of the above assumptions, H_2O, is the correct one, and that the relative weights of the hydrogen and oxygen atoms are as 1 to 16. We have reason also to believe that the molecule of litharge contains 1 atom each of lead and oxygen, as represented by the formula PbO, the weights being in the ratio of 207 to 16, corresponding to the ratio 1 to 0.0772 given on p. 34. Red lead, where we have 3 times this amount of lead and 4 times this amount of oxygen, would accordingly be represented by the formula Pb_3O_4, and lead dioxide, where the proportion of oxygen to lead is twice that in litharge, would correspond to the formula PbO_2.

Numerical Values of Atomic Weights. The actual weights of the atoms are exceedingly small, expressed in ordinary units, such as grams,* and it is far more convenient to select a much smaller weight as unit, such as the weight of one of the atoms themselves. It is purely arbitrary which atom

* It would take approximately 3×10^{23} atoms of hydrogen to weigh 1 g.

we choose and what number we assign to it, so long as we select corresponding values for the other atoms. Thus, knowing that the molecule of water contains 8 times as much oxygen as hydrogen, and granting that H_2O is the correct formula for it, we might call O = 100, when H must be 6.25; or again, if we let O = 1, then H = 0.0625, etc.

The choice appeared a very simple one to most early chemists, who, finding that the atoms of hydrogen are lighter than those of any other known element, decided to call its weight 1, making O = 16, and making the weights of the atoms of other substances to be expressed by numbers greater than 1. More recently it has been found that the ratio of weights of the atoms of hydrogen and oxygen is not exactly 1 to 16, but 1 to 15.88, and that if we take O = 16 as our unit, making H = 1.0076, the atomic weights of most of the other elements come out much nearer whole numbers than if we let H = 1 and O = 15.88. This is illustrated by the following sets of values based on the two assumptions.

Hydrogen	1.0076	1.000
Oxygen	16.00	15.88
Calcium	40.07	39.77
Carbon	12.01	11.91
Lithium	6.94	6.89
Magnesium	24.32	24.14
Nitrogen	14.01	13.90
Phosphorus	31.04	30.81
Potassium	39.10	38.80
Sodium	23.00	22.83
Sulfur	32.06	31.76

A still greater reason for the choice of O = 16.00 lies in the fact that but few of the elements form compounds with hydrogen, while nearly all form compounds with oxygen, and hence the atomic weight ratio between an element and oxygen can be determined directly, while the atomic weight ratio between the element and hydrogen could only be indirectly determined, and would therefore be subject to more frequent change.

Interpretation of Formulas. We are now prepared to interpret the notation used by chemists to indicate the composition of pure substances, though we have not yet shown that actual compounds have the composition assigned to them. We find the atomic weights given with the names and symbols of the elements on p. 13, indicating the weight of each atom in terms of a unit which is one sixteenth the weight of an oxygen atom. The smallest part of any compound, the **molecule**, is thus made up of atoms of its component elements, with corresponding weights. This molecule is indicated by a **formula** showing the number and kind of atoms of which it is composed. Thus the formula Fe_2O_3 indicates a molecule of a certain oxide of iron containing 2 atoms of the element iron, which constitute 2×56 parts by weight, together with 3 atoms of the element oxygen, which constitute 3×16 parts by weight. Another formula, Fe_3O_4, represents another oxide of iron, containing 3 atoms of iron to 4 atoms of oxygen, the weights being in the ratio 3×56 to 4×16. Na_2CO_3 denotes 1 molecule of sodium carbonate, "washing soda," containing 2 atoms or 2×23 or 46 parts of sodium, 1 atom or 12 parts of carbon, and 3 atoms or 3×16 or 48 parts of oxygen, the whole molecule representing 106 parts.

Gram-Atoms and Gram-molecules, or Mols. Although we reason in terms of atoms and molecules, we work with vastly larger amounts of material, and it is often convenient to give a slightly different meaning to our symbols and formulas so as to express parts by weight in terms of units actually used. Accordingly the symbol Fe is often used to denote not a single atom of iron, but 56 **grams** of iron, called a **gram-atom** of iron. Likewise the formula Fe_2O_3 denotes not only a single molecule of an oxide of iron, but a **gram-molecule**, or **mol**, of the oxide, weighing 160 g. Since one molecule of the oxide contains 112 parts of iron to 48 parts of oxygen, then no matter how many molecules of the oxide we take, the proportion of iron to oxygen is still 112 to 48, hence the same weight relations that apply to atoms and molecules apply to gram-atoms and gram-molecules. The adjective **molal** is used in referring to the properties of the mol. Thus we would refer to the molal weight of Fe_2O_3 as being 160 g.

This numerical significance of chemical formulas aids us in solving problems involving the relative weights of compounds and their component elements. Suppose that we wished to calculate the amount of litharge that might be made from 1 kg. (1000 g.) of lead. Since one atom of lead, representing 207 parts by weight, combines with one atom of oxygen, representing 16 parts by weight, to give a molecule of litharge, PbO, representing 223 parts by weight, we can say that

207 parts of lead will give 223 parts of litharge,

and accordingly 207 g. of lead will give 223 g. of litharge,

and 1 g. of lead will give 1.0772 g. of litharge,

and 1000 g. of lead will give 1000×1.0772 g. of litharge, or 1077.2 g.

Chemical Equations. When a chemical reaction takes place there is a rearrangement of atoms into new groups, or molecules, forming new substances. This is indicated by a **chemical equation**, in which the rearrangement is shown by the regrouping of the atomic symbols to represent the new molecular species formed. For example, the formation of iron and carbon dioxide, CO_2, from the ore Fe_2O_3 by the action of carbon monoxide, CO, is represented by the equation,

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2.$$

The following things may be noted about such an equation:

First, an equation tells nothing about the conditions necessary for carrying out the reaction, and the mere writing of an equation does not imply that the reaction it represents will actually be realized.

Second, it must represent the fact that no matter disappears, by showing the same number of atoms of each element on both sides of the equation, though they are arranged in different molecules.

Third, it represents the relative number of molecules of each substance taking part in the reaction.

Fourth, it represents the relative weights of each substance, which can be readily completed with the aid of the table of atomic weights.

The above equation, then, may be read as follows: 1 molecule of ferric oxide reacts with 3 molecules of carbon monoxide to yield 2 molecules (or atoms) of iron and 3 molecules of carbon dioxide; also, $2 \times 56 + 3 \times 16$ parts (by weight)

of iron oxide react with $3(12 + 16)$ parts of carbon monoxide to give 2×56 parts of iron and $3(12 + 32)$ parts of carbon dioxide. These parts by weight may be in any kind of weight unit, pounds, tons, ounces, grams, etc. In accordance with our double usage of the symbols and formulas to represent not only single atoms and molecules, but also gram-atoms and gram-molecules, or mols, as explained on p. 41, we often read an equation in terms of grams; hence, 160 g. of iron oxide, when reacting with 84 g. of carbon monoxide, give 112 g. of iron and 132 g. of carbon dioxide, which quantities represent 1 mol, 3 mols, 2 mols and 3 mols respectively.

This may be summarized briefly by writing under each formula in the equation its complete meaning in both of the above senses.

	Fe_2O_3	+ 3 CO	= 2 Fe	+ 3 CO_2
(1) Number of molecules	1	3	2	3
Weight, in terms of one sixteenth the weight of an oxygen atom	160	84	112	132
(2) Number of mols	1	3	2	3
Weight	160 g.	84 g.	112 g.	132 g.

Calculation of Weight Relations. The meaning thus attached to chemical formulas and equations makes it possible to calculate the weights of all the other substances involved in a chemical reaction from the weight given for any one of them. Suppose, for example, that it is required to find the weight of iron that should be obtained from 100 lb. of the oxide of iron considered above. From the weights implied by the formulas, as explained above, we may say,

160 parts (pounds) of Fe_2O_3 will give 112 parts (pounds) of iron, hence 1 part (pound) of Fe_2O_3 will give $\frac{112}{160}$ parts (pounds) of iron, and 100 parts (pounds) of Fe_2O_3 will give $\frac{100\times112}{160}$ parts (pounds) of iron, or 70 parts (pounds) of iron.

Again, suppose we wish to find the amount of coke, containing 80 per cent carbon, the rest being ash, that is required to reduce to iron the above amount of ore. From the weights implied in the equation, we can say that

160 lb. of oxide will require 36 lb. of carbon (which would first burn to 84 lb. of CO), hence 1 lb. of oxide will require $\frac{36}{160}$ lb. of carbon, and 100 lb. of oxide will require $100 \times \frac{36}{160}$, or 22.5 lb. of carbon. Since, further, this amount of carbon is 80 per cent of the coke required, the amount of the latter is $\frac{100}{80}$ of 22.5 lb., or 28.1 lb.

This connection between atomic weights, formulas and relative weights of substances may be used not only to calculate the relative weights from the formulas and atomic weights, as above, but also to calculate the atomic weights when the formulas and suitable weight relations are known, or again, to determine formulas when the other two factors are known.

Calculation of Atomic Weights. As an example of the calculation of atomic weights let us suppose that we know the formula of a certain oxide of copper to be Cu_2O and find on analysis that 0.5120 g. of it contains 0.4548 g. of copper, and wish to calculate the atomic weight of copper. The formula tells us that 2 atoms of copper are combined with 1 atom of oxygen, hence there would be 2 gram-atoms of copper to 1 gram-atom of oxygen. Since there are, according to the analysis, 0.4548 g. of copper to 0.0572 g. of oxygen, there would be $\frac{16\times0.4548}{0.0572}$ g., or 127.2 g. of copper to 1

gram-atom (16 g.) of oxygen. Since 127.2 g. of copper is 2 gram-atoms, 1 gram-atom is 63.6 g. Hence the atomic weight of copper is 63.6.

Calculation of Formula. The third case consists in calculating the formula when the other two factors, atomic weight and composition, are known. Suppose that we find on analysis that a certain chloride of arsenic contains 58.68 per cent of chlorine, and know the atomic weight of arsenic, As = 75.0, and chlorine, Cl = 35.5, and wish to determine the formula of the compound. Now the formula indicates primarily the relative number of atoms, or of gram-atoms, in the molecule, or mol, respectively, so that we may proceed to determine the number of gram-atoms of one element combined with 1 gram-atom of the other. Since 58.68 g. of chlorine would combine with 41.32 g. of arsenic, 35.5 g. of chlorine, 1 gram-atom, would combine with $\frac{35.5 \times 41.32}{58.68}$ g., or 25.0 g., of arsenic, which is $\frac{1}{3}$ gram-atom of arsenic. We cannot have $\frac{1}{3}$ atom of arsenic, so that we conclude, from the fact that 1 gram-atom of chlorine would combine with $\frac{1}{3}$ gram-atom of arsenic, that 3 atoms of chlorine would combine with 1 atom of arsenic, hence the formula is $AsCl_3$ or some multiple of it, such as As_2Cl_6, As_3Cl_9, etc. To distinguish between these multiples another kind of data is necessary. This will be considered in Chapter IV.

EXERCISES

1. What do you understand by the law of simple multiple proportions?

2. How does the atomic theory explain this law?

3. Write out in words all that the following formulas mean to you: H_2O; H_2O_2; $Ca(OH)_2$; $FeSO_4$.

4. Define symbol, formula, chemical reaction, chemical equation, mol, molecule, atom.

5. How many pounds of iron are there in 100 pounds of magnetic iron ore, Fe_3O_4? *Ans.* 72.4 lb.

6. How many grams of sodium peroxide (Na_2O_2) can be obtained from 115 g. of sodium? *Ans.* 195 g.

7. When treated with hydrochloric acid, barium peroxide yields hydrogen peroxide according to the following equation:

$$BaO_2 + 2\ HCl = H_2O_2 + BaCl_2.$$

How much BaO_2 is required to make 10 lb. of a 5 per cent solution of H_2O_2? *Ans.* 2.5 lb.

8. On heating 58 g. of silver oxide, Ag_2O, it was decomposed into oxygen gas and 54 g. of metallic silver. What is the atomic weight of silver, if that of oxygen is 16? *Ans.* 108.

9. How many grams are there in 1 mol of each of the following substances: $Ca(OH)_2$; HCl; NaCl?

Ans. 74 g.; 36.5 g.; 58.5 g.

10. 10 g. of limestone, $CaCO_3$, was put into a closed vessel and heated to such a temperature that 2 per cent of it decomposed according to the equation, $CaCO_3 = CaO + CO_2$. How many grams of CO_2 were produced? *Ans.* 0.088 g.

11. A certain oxide of nitrogen was found by analysis to contain 74.1 per cent of oxygen. Work out its simplest formula.

CHAPTER IV

VOLUME OF GASES. MOLECULAR WEIGHTS

Choice of Formulas and Corresponding Atomic Weight. In the last chapter we showed how the atomic theory, deduced from the law of conservation of mass and the law of simple multiple proportions by weight, could be expressed in a simple and comprehensive notation by the aid of which any one of the three factors, relative weights, formula and atomic weights, could be calculated from the other two. Now the relative weights may be found by experiment, but in order to get either of the other factors one of them must be known. Although we practiced with a number of formulas to become familiar with the meaning of the notation used, we did not show that the molecules of the substances referred to actually contained the numbers of atoms of the constituent elements signified by the formulas used, *e.g.*, H_2O, Fe_2O_3, $AsCl_3$.

To illustrate the problem we now face let us consider the formula of water. We know thus far only that the ratio of the weight of hydrogen to that of oxygen in water is approximately 1 to 8. This we learn by the analysis of water. If, now, the formula of water is HO, the relative weights of the atoms of hydrogen and oxygen are 1 to 8. But if the molecule of water is to be represented by H_2O, the relative weights of the single atoms would have to be 1 to 16. Again, if the formula is HO_2, then the relative atomic weights must

be 1 to 4. Evidently we must bring to bear some criteria other than those thus far considered, in order to select the correct formula and atomic weight ratio.

If we should try to represent the formation of water from its elements on the basis of the various assumptions as to its formula, we should have, as probable guesses, equations such as the following:

$$\begin{aligned} H + O &= HO, \\ 2\,H + O &= H_2O, \\ H + 2\,O &= HO_2, \text{ etc.} \end{aligned}$$

By suitable choice of atomic weights any of these, or others, as just explained, would conform to the experimental weight ratio. The essential point of difference lies in the number of molecules of the three substances.

Now we have, from the kinetic theory, a means of measuring the relative numbers of molecules for gaseous substances. It was shown in Chapter II that, by Avogadro's Rule, at equal temperatures and pressures, equal volumes of all gases contain the same number of molecules. Accordingly, if we determine the relative volumes of the gases taking part in a chemical reaction, in which the temperature and the pressure are the same before and after the experiment, we may conclude that the relative numbers of molecules are in the same proportion as the volumes. If the above reaction is carried out at a temperature high enough to keep the water in the vapor state, it will be found that two volumes of hydrogen and one volume of oxygen give two volumes of steam. Accordingly, we conclude that two molecules of hydrogen and one molecule of oxygen would give two molecules of steam. Our equation must now be

written so as to express these numbers of molecules. **Since the oxygen in one molecule is enough to give two molecules of steam, each containing oxygen, there must be more than one atom of oxygen in its molecule**, hence its formula must be not O but O_2, or O_4, etc. However, as we consider other reactions, we never find that one molecule of oxygen gives more than two molecules of any other substances, so we assume the simplest formula, O_2. This limits the above equation to the following:

$$2\,H_n + O_2 = 2\,H_nO,$$

where n is some whole number.

We still have to determine the number of atoms in the molecule of hydrogen. This is done, as in the case of oxygen, by finding the greatest number of other molecules, each containing hydrogen, that can be obtained from one molecule of hydrogen. This number has never been found greater than two, but often equal to two, hence we write H_2. The union of hydrogen and chlorine to form hydrogen chloride gas may be used for illustration. Experiment shows that one volume of hydrogen and one volume of chlorine give two volumes of hydrogen chloride, hence one molecule of hydrogen and one molecule of chlorine give two molecules of hydrogen chloride, and the equation would be

$$H_2 + Cl_2 = 2\,HCl.$$

Using this formula for hydrogen in our previous example, we write the equation for the formation of water

$$2\,H_2 + O_2 = 2\,H_2O.$$

Finally, knowing the relative weights by experiment, and having deduced the formulas by the aid of Avogadro's

Rule, we can assign values to the atomic weights. As explained before, one of these must be chosen arbitrarily, and we have seen how the number 16 has been assigned to the oxygen atom. Using this value, the weight of the oxygen molecule, O_2, becomes 32. By analysis of water we find that 32 parts of oxygen combine with 4.030 of hydrogen. The above equation shows that this represents four gram-atoms of hydrogen, hence one gram-atom of hydrogen is 1.008 g., and this number represents the atomic weight of hydrogen.

It is not long since the time when the simple way just explained for deciding upon the correct formula and atomic weight ratio was not understood. Many chemists, as late as 1858, used HO for the formula of water, while others used H_2O, and much confusion existed. Many criteria were used, other than those furnished by gas volumes, to determine the true formulas, but with only partial success. The table of atomic weights is thus the product of the thought and experimental work of a great many men.

We have seen that the molecules of hydrogen, oxygen and chlorine each contain two atoms. The same is true for nitrogen, fluorine, bromine and iodine. Another variety of oxygen exists, called ozone, formed from oxygen by the silent electric discharge, with a diminution in volume in the ratio of 3 to 2, indicating that the equation must be written

$$3\ O_2 = 2\ O_3.$$

The molecule of ozone, therefore, contains three oxygen atoms. The molecule of phosphorus vapor at low temperatures is P_4, at higher temperature P_2, that of sulfur may be S_8, S_6, S_4 or S, according to the temperature. When metals

are vaporized their molecules seem always to consist of single atoms. The same is true of argon, and certain other gases recently discovered existing in small amounts in the atmosphere.

Changes in Volume or Pressure in Gas Reactions. The connection we have traced between the volumes of gases in chemical reactions and the relative number of molecules may be used conversely to deduce the change of volume or pressure to be expected when reactions take place between substances whose formulas are known. Consider, for example, the reaction represented by the equation

$$2\,SO_2 + O_2 = 2\,SO_3.$$

If this reaction is carried out at a temperature at which all of the substances represented are gaseous, then we see that three molecules have formed two. If the temperature and volume have been kept the same during the reaction, this will result in a decrease of the pressure to two thirds of its former value. If the temperature and pressure are the same as before, then the volume will be two thirds of its former value.

It is important, whenever an equation will be used to deduce relative volumes, to use the correct formulas of the substances in the gaseous form. For example, the same weight, 28 g., is indicated both by N_2 and 2 N, but the second formula is incorrect, and would lead us to expect twice the volume which would actually be involved.

Volume of One Mol of Any Gas. The double meaning attached to chemical symbols and formulas was explained in Chapter II, one referring to single atoms and molecules, and furnishing a basis for reasoning, and the other referring

to the gram-atom and gram-molecule, or mol, and furnishing a basis for experimental work. Having determined that equal numbers of gaseous molecules are contained in equal volumes, at equal temperatures and pressures, and that the mol of all substances consists of the same number of molecules, it becomes important to ask what is the actual volume occupied by the mol of gas. This rests upon the measurement of gas densities, as illustrated by the following table:

Gas	Wt. of 1 liter 0° C., 1 atmos.	Vol. of 1 g. 0° C., 1 atmos.	g. per mol	Vol. of 1 mol 0° C., 1 atmos.
H_2 . .	0.08988 g.	11.126 liters	2.016	22.43 liters
O_2 . .	1.4291 g.	0.6998 liter	32.00	22.39 liters
N_2 . .	1.2507 g.	0.7995 liter	28.02	22.40 liters
NH_3 . .	0.7621 g.	1.3122 liters	17.03	22.35 liters

These values for the volume of the mol of gas under standard conditions, as well as others that might be added, are all very close to 22.4 liters, which may therefore be selected as the molal volume of a gas under standard conditions. (This is the volume of a cube 28.2 cm. or $11\frac{1}{8}$ inches on the side.) We may take this volume as the basis of our working definition of molecular weight, saying that the molecular weight of a substance is the number of grams of it which occupy 22.4 liters when it is in the gaseous form and under standard conditions. Very frequently, of course, substances cannot exist in the vapor state under these conditions, so that the relation between the weight and the volume of vapor must be found experimentally at some higher temperature, and perhaps lower pressure, after which it is possible to calculate the weight that 22.4 liters

of the vapor would have at 0° C. and 1 atmosphere, if no condensation took place.

We may illustrate by examples the various types of problems it is possible to solve with the aid of this relationship.

1. **Calculation of the Weight of a Given Volume or the Volume of a Given Weight of a Gas.** Example: What is the volume of 10 g. of O_2 at 127° C. and 0.5 atmosphere? The answer to this is obtained by the following obvious steps.

32 g. of O_2 occupy 22.4 liters at 273° A. and 1 atm.

32 g. of O_2 occupy 44.8 liters at 273° A. and 0.5 atm.

32 g. of O_2 occupy $\frac{400}{273} \times 44.8$ liters at 400° A. (127° C.) and 0.5 atm.

1 g. of O_2 occupies $\frac{1}{32} \times \frac{400}{273} \times 44.8$ liters at 400° A. and 0.5 atm.

10 g. of O_2 occupy $\frac{10}{32} \times \frac{400}{273} \times 44.8$ liters or 20.5 liters at 400° A. and 0.5 atm.

Example: What is the weight of 50 liters of CO_2 measured at 25° C. and 3 atm.?

At 273° and 1 atm. 22.4 liters of CO_2 weigh 44 g.

At 273° A. and 3 atm. $\frac{1}{3} \times 22.4$ liters of CO_2 weigh 44 g.

At 298° A. (25° C.) and 3 atm. $\frac{298}{273} \times \frac{1}{3} \times 22.4$ liters, or 8.16 liters, of CO_2 weigh 44 g.

At 298° A. and 3 atm. 1 liter of CO_2 weighs $\frac{44}{8.16}$ g.

At 298° A. and 3 atm. 50 liters of CO_2 weigh $50 \times \frac{44}{8.16}$ g., or 270 g.

2. **Determination of the Relative Weights of a Gas and Air.** It is often important to know whether a gas is heavier or lighter than air. The proportion of nitrogen to oxygen in air is very nearly 4 to 1 by volume, so that in 22.4 liters

of air four fifths of the molecules would be nitrogen and one fifth would be oxygen. Taking four fifths of 22.4 liters of nitrogen under standard conditions, weighing four fifths of 28.0 g., and mixing it with one fifth of 22.4 liters of oxygen, weighing one fifth of 32.0 g., we would get 22.4 liters of air weighing 28.8 g., under standard conditions. Suppose we wish to know the relative density of the following gases with respect to air: CO_2, NH_3, HCl, Cl_2. We can find their molecular weights with the aid of the atomic weight table, and conclude that 22.4 liters under standard conditions would have the following weights: CO_2, 44 g.; NH_3, 17 g.; HCl, 36.5 g.; Cl_2, 70 g.; air, 28.8 g. This shows at once the relative weight of each with respect to the air.

3. **Determination of Molecular Weight.** Example: What is the molecular weight of phosphorus vapor and what is its formula, given the atomic weight, P = 31.0, and the experimental determination that a flask having a volume of 583 cc. was filled with the vapor at 310° C. and a pressure of 756 mm., and that it was found on cooling to contain 1.49 g. of phosphorus? The molecular weight is found from the number of grams occupying 22.4 liters at 273° A. and 760 mm., which must therefore be calculated.

Since 1.49 g. of phosphorus vapor occupied 583 cc. at 756 mm. and 583° A.,

1.49 g. of phosphorus vapor would occupy $\frac{756}{760} \times 583$ cc. at 760 mm. and 583° A.,

1.49 g. of phosphorus vapor would occupy $\frac{273}{583} \times \frac{756}{760} \times 583$ cc. at 760 mm. and 273° A.,

1.49 g. of phosphorus vapor would occupy 0.2715 liter at 760 mm. and 273° A.,

$\frac{22.4}{0.2715} \times 1.49$ g., or 123 g., of phosphorus vapor would occupy 22.4 liters at 760 mm. and 273° A.

Since 123 g. would occupy 22.4 liters under standard conditions, if it did not condense, 123 is approximately the molecular weight. Since the atomic weight is 31, there are evidently 4 atoms in the molecule, so that the formula is P_4.

As another example we may determine the formula of a compound, found by analysis to contain 40 per cent of carbon, 6.67 per cent of hydrogen, and 53.33 per cent of oxygen, and of which 0.50 g. gave 328 cc. of vapor at 200° C. and 750 mm. We will first find the relative number of atoms of each element in the molecule of the compound. From the per cents given we may say that

40 g. of carbon combine with 6.67 g. of hydrogen and 53.33 g. of oxygen, therefore 12 g. of carbon combine with $\frac{12}{40}$ of 6.67 g. or 2 g. of hydrogen and $\frac{12}{40}$ of 53.33 g. or 16 g. of oxygen. Since 12 g. of carbon, 2 g. of hydrogen and 16 g. of oxygen are 1 gram-atom of carbon, 2 gram-atoms of hydrogen and 1 gram-atom of oxygen respectively, these represent the relative numbers of atoms of the three elements in the molecule. The formula might therefore be CH_2O. However, the same proportions by weight would be found if the formula were $C_2H_4O_2$ or $C_3H_6O_3$, or any other multiple of CH_2O. In order to distinguish between them we must therefore determine the number of grams per mol, which is numerically equal to the molecular weight.

Since 0.5 g. occupy 328 cc. at 750 mm. and 473° A.(200° C.), 0.5 g. would occupy $\frac{750}{760} \times 328$ cc. at 760 mm. and 473° A., and 0.5 g. would occupy $\frac{273}{473} \times \frac{750}{760} \times 328$ cc., or 187 cc. at 760 mm. and 273° A.

Now the weight of gas contained in 22.4 liters, or 22,400 cc., is 1 mol, and since 187 cc. weigh 0.5 g., 1 cc. would weigh 0.00267 g. and 22,400 cc. would weigh $22{,}400 \times 0.00267$ g., or 60 g. Of the various multiples of CH_2O the one having a molal weight of 60 g. is $C_2H_4O_2$, hence this is the correct formula.

4. **Direct Relation between Volumes of Gases and Weights of Other Substances in Reactions.** Example: when limestone is heated to a sufficiently high temperature, it decomposes, as represented by the following equation:

$$CaCO_3 = CaO + CO_2.$$

Suppose we wish to calculate how many liters of CO_2, measured at 20° C. and 10 atmospheres pressure, should be obtained from 2 kilograms (2000 g.) of $CaCO_3$. It is not necessary to calculate the weight of CO_2, since the equation can be interpreted so as to give directly the relation between the weight of $CaCO_3$ and the volume of CO_2. From 1 mol of $CaCO_3$ weighing 100 g. there can be obtained 1 mol of CO_2 occupying 22.4 liters at 273° A. and 1 atmos. Accordingly, 2000 g. $CaCO_3$ would give 448 liters CO_2 at 273° A. and 1 atmos., or $\frac{293}{273} \times 448$ liters at 293° A. and 1 atm., or $\frac{1}{10} \times \frac{293}{273} \times 448$ liters or 41.7 liters of CO_2 at 293° A. and 10 atmos.

Complete Interpretation of Chemical Equations. It is possible now to summarize what has been presented in this chapter and the preceding one concerning the interpretation of chemical equations, both as to weight and volume relations, bearing in mind that a formula always signifies a certain weight of some substance, and, when the substance exists in the gaseous state, a certain volume under standard

conditions. We may recall that formulas are interpreted in two ways, one referring to atoms and molecules, the other to gram-atoms and gram-molecules, or mols. This double interpretation may be illustrated by using an equation as in the following table, writing under each formula its significance in both senses.

	CO_2 (gas) + C (solid) = 2 CO (gas)		
(1) Weights in terms of oxygen atom = 16	44	12	56
Number of molecules	1	1	2
Relative volumes	1	0 +	2
(2) Weight in grams	44	12	56
Number of mols	1	1	2
Volume at 0° C., 1 atm.	22.4 liters	$\frac{12}{\text{density}}$ cc.	44.8 liters
Number of molecules	6×10^{23}	6×10^{23}	12×10^{23}

The last row of figures is added for the sake of interest, not because it will be used in problems. The other data represent all that is necessary in order to solve any problem involving weights, or volumes of gases, provided that one knows how to apply the gas laws to get the relation between the volumes of gases at standard conditions and at other conditions. It must be noted that this generalization connecting weights and volumes is possible only where gases are involved. With liquids and solids the densities of the particular substances must be determined by experiment.

Molecular Weights of Dissolved Substances. It is frequently impossible to determine the molecular weight of a substance from the volume of its vapor, owing to decomposition on heating. Sugar, for example, decomposes instead of vaporizing when heated, turning first to caramel and then charring. Some property other than the density in the vapor state is therefore necessary in order to determine its molecular weight, and to decide which multiple of its empirical formula, $C_{12}H_{22}O_{11}$, is the correct one. Hydrogen peroxide, likewise, is very unstable, except when in a dilute solution, decomposing often with explosive violence when in the pure state. Analysis shows that it contains twice as much oxygen in proportion to the hydrogen as does water, hence, having decided that water is represented by the formula H_2O, we may conclude that hydrogen peroxide must be represented by one of the formulas HO, H_2O_2, H_3O_3, etc. These are alike in the proportion of hydrogen to oxygen, 1 to 16, but differ in the total weight of the molecule, *i.e.*, the molecular weight. To distinguish between these possible formulas, therefore, we must find out whether the mol weighs 17 g. or 34 g. or 51 g., etc. For such substances the molecular weight must be determined under conditions such that the substance does not decompose, which is the case often in dilute solutions.

Among the properties of a solution which depend upon the molecular weight of the dissolved substance (called the solute) are the vapor pressure, the boiling point and the freezing point. To understand the nature of the effect of a solute we may apply again the kinetic theory. If we have a pure liquid in contact with its vapor in a closed vessel, we imagine that there is a constant interchange of

molecules between the two phases, molecules going from the liquid into the vapor phase at the same rate that others go from the vapor phase back into the liquid. If now, keeping the temperature constant, we add to the liquid in the closed vessel some molecules of another kind which are not volatile, and so cannot escape into the vapor phase, the number of molecules capable of escaping from the solution is now less than before, resulting in a smaller pressure of vapor above the liquid. If the new molecules introduced are attracted in about the same way as the molecules of solvent originally present, then we might expect that if the volatile molecules of solvent constitute, say, only 0.9 of the total number of molecules, their vapor pressure would be only 0.9 of what it is when the solvent is pure. This conclusion is borne out by experiment. This may be used to determine molecular weights, for if we find that a certain number of grams of solute in a certain number of mols of solvent lower the vapor pressure of the latter to, say, 0.9 of its value when the solvent is pure, then 0.9 of the total number of molecules are of the solvent and 0.1 are of the solute, from which we can calculate the number of grams per mol of solute.

Example: Pure carbon disulfide, CS_2, has a vapor pressure of 297 mm. at 20° C. It was found by experiment that 12.7 g. of iodine dissolved in 38 g. of CS_2 lowered the vapor pressure of the latter to 270 mm. Given the atomic weight, 127, we wish to know the formula of dissolved iodine. Since 270 mm. is 0.909 of 297 mm., the number of mols of CS_2 is now 0.909 of the total number, and the number of mols of iodine is therefore 0.091 of the total number, or 0.1 of the number of mols of CS_2. One mol of CS_2 weighs

76 g., and therefore 38 g. is 0.5 mol. Since there are 0.1 as many mols of iodine as of CS_2, or 0.05 mol, then 12.7 g. of iodine is 0.05 mol, and 254 g. is 1 mol. Since the gram-atom of iodine is 127 g., there are 2 gram-atoms per mol, and hence 2 atoms per molecule, so that the formula is I_2.

Instead of measuring the number of dissolved mols by the lowering of the vapor pressure of the solvent, the temperature being kept the same, we may, on the other hand, keep the pressure the same, say 1 atmosphere, and determine how much the temperature must be increased in order to make the vapor pressure of the solvent great enough to continue boiling, *i.e.*, we may measure the rise in the boiling point produced by the added solute. Although the relation between this rise and the number of mols of solute is not so obvious as that between the lowering of vapor pressure and the number of mols of solute, it is probably evident that it is only the number of added mols and not their kind that determines the rise in the boiling point, so that having determined this effect for one solute of known molecular weight, we can use it to determine the molecular weight of other solutes.

Just as it is harder to vaporize the solvent from a solution than it is from the pure solvent, so it is harder to remove it by any other means, such as freezing, and just as the boiling point of a solution of a non-volatile substance is higher than that of the solvent, so the freezing point of the solution will be lower, and will depend, likewise, only on the number of mols of solute in a given amount of solution. In addition, therefore, to defining a mol experimentally as the number of grams which, in the vapor state and under standard conditions, would occupy 22.4 liters, we may also define a mol

as the number of grams which, dissolved in a specified amount of some solvent, will cause a certain rise in the boiling point or lowering in the freezing point. For water as solvent, the rise in boiling point is 0.52°, and the lowering in the freezing point is 1.86°, when 1 mol of any solute is contained in 1000 g. of water. For other concentrations the effect is nearly proportional. These numbers have been calculated from the heats of vaporization and fusion, but the explanation of the method lies beyond the scope of this book. Confirmation is found in the fact that a substance like alcohol, which can exist both as vapor and in aqueous solution, gives approximately the same molal weight by both methods.

Example: It was found that a solution of 7.29 g. of sugar in 100 g. of water had a freezing point 0.395° lower than that of water. What is the molecular weight of the sugar? For each 1000 g. of water in a solution of the same concentration there would be 72.9 g. of sugar. Now, 1 mol of sugar in this amount of water would produce a lowering of 1.86°, and since 72.9 g. produces a lowering of only 0.395°, which is $\frac{0.395}{1.86}$ or 0.213 of the lowering produced by 1 mol, there must be only 0.213 of a mol present. If, then, 72.9 g. is 0.213 mol, 1 mol is $\frac{72.9}{0.213}$ g. or 342 g. Comparing this with the empirical formula of sugar given on p. 58, $C_{12}H_{22}O_{11}$, as determined by analysis, we see that the simplest formula is the correct one.

EXERCISES

1. It is found by experiment that 3 vols. of hydrogen and 1 vol. of nitrogen are produced by the decomposition of 2 vols. of ammonia. If the molecules of hydrogen and nitrogen have been determined to be H_2 and N_2 respectively, what must be the formula of ammonia?

2. What are the relative volumes of the gases represented by the following equations:

$$2\ CO + O_2 = 2\ CO_2;$$
$$2\ H_2S + 3\ O_2 = 2\ H_2O + 2\ SO_2.$$

3. Write equations expressing the combustion, to CO_2 and H_2O, of two samples of gasoline consisting supposedly of C_6H_{14} and C_8H_{18} respectively. (*a*) What volume of oxygen is required per volume of vapor in each case? (*b*) What approximate volume of air? *Ans.* (*a*) 9.5, 12.5; (*b*) 47.5, 62.5.

4. What is the weight of 22.4 liters of each of the following gases under standard conditions: N_2, CO, H_2S, NH_3, HCl, NO? *Ans.* 28 g., 28 g., 34 g., 17 g., 36.5 g., 30 g.

5. If we consider air as a mixture of one fifth oxygen and four fifths nitrogen, by volume, what is the weight of 22.4 liters of it? *Ans.* 28.8 g.

6. Which of the gases in question 4 are heavier and which lighter than air?

7. What is the volume of 10 g. of hydrogen, (*a*) under standard conditions, (*b*) at 546° C. and 10 atmos.? *Ans.* (*a*) 112 liters; (*b*) 33.6 liters.

8. How many grams of oxygen are in a tank having a volume of 5 liters, with a pressure of 10 atmos. and the temperature 27° C.? *Ans.* 65 g.

9. How many liters of CO_2, measured at 77° C. and 2 atmos., could be produced from 2 kilograms of $CaCO_3$? *Ans.* 287 liters.

10. A bulb having a capacity of 450 cc. weighs 20.155 g. when empty. It is then filled with a certain gas at a temperature of 177° C. and a pressure of one atmos. The weight when filled with gas is found to be 21.170 g. What is the molecular weight of the gas? *Ans.* 83.

11. A certain gas is known to have a formula of the type CH, C_2H_2, etc. Given that 295 cc. of it weigh 0.317 g. at 22° C. and 1 atmos., which formula is correct?

12. What would be the relative efficiency of hydrogen, H_2, and methane, CH_4, in raising a balloon? *Ans.* 2.1 to 1.

13. Hydrogen peroxide contains 1 part by weight of hydrogen to 16 parts of oxygen, and a solution of 0.369 g. of it in 25 g. of water had a freezing point of $-0.805°$. What is its formula?

Ans. H_2O_2.

14. The vapor pressure of pure chloroform, $CHCl_3$, is 370 mm. at 40° C. What will it become if 6.40 g. of naphthalene, $C_{10}H_8$, is dissolved in 239 g. of $CHCl_3$? *Ans.* 361 mm.

CHAPTER V

TYPES OF CHEMICAL COMPOUNDS

Relation between Stability of Compounds and Metallic or Non-metallic Character of Their Constituent Elements. On examining the known chemical compounds containing but two elements, the binary compounds, it is found that they represent the large majority of the possible pairs of elements, so that nearly all of the elements are capable of chemical union with each other. There is, however, a great difference in the nature and stability of the compounds formed, depending on the nature of the constituent elements. For example, oxygen and fluorine form no compound, oxygen and chlorine form two unstable compounds, easily decomposed by heating, and oxygen and zinc form a very stable compound. On examining a large number of binary compounds in this way we find usually that those which are most stable are composed of a metallic and a non-metallic element. In Chapter I the physical properties differentiating metals and non-metals were discussed. We will now see that these physical differences are accompanied by fundamental differences in chemical behavior. As was pointed out, there is no sharp dividing line between the metals and non-metals, but rather they grade into each other. Accordingly it is quite logical to speak of one element as being more or less metallic than another, and we might make an attempt to arrange them in the order of their metallic character. It is impossible to make such

an arrangement very strict, for the order would vary somewhat according to the criterion chosen. This difficulty does not, however, prevent the notion of the rôle of metallic character in chemical combination from being an exceedingly useful one. As an illustration we may give the following list which contains a few of the commoner elements, ranging from those which are extremely metallic, at the top, to the opposite extreme of those least metallic at the bottom.*

The "Alkali Metals," Potassium, Sodium, etc.
The "Alkaline Earth Metals," Barium, Calcium, etc.
Aluminum, Magnesium, Zinc.
Iron, Nickel, Tin, Lead.
Hydrogen.
Copper.
The "Noble Metals," Silver, Gold.
Sulfur.
Iodine.
Chlorine.
Oxygen, Fluorine.

The most stable compounds are usually those formed between elements far apart on this list. The alkali metals unite with elements like oxygen and chlorine very eagerly, with the evolution of a great deal of heat, and these compounds require a great deal of energy for their decomposition. The resulting compounds, furthermore, are very unlike their component elements. Sodium chloride, common salt, bears no resemblance, physical or chemical, to its component elements. On the other hand, elements near together, like chlorine and oxygen, or chlorine and iodine,

* A fuller discussion of the relative metallic character of the individual elements will be found in Chapters XVI and XVII.

form compounds very similar in properties to their component elements, and which are readily broken down. The metals form numerous compounds with each other, but usually very little energy is involved in the process, unless the metals are very different, like mercury and sodium, and in many cases the compounds are much like the constituent elements in character. Hydrogen is, chemically, rather more like a metal than it is like a non-metal, as it forms compounds only with the most strongly metallic metals, and these are easily decomposed, whereas it combines with the non-metals to form compounds of increasing stability as we descend the list.

Since it is usually possible to regard one of the elements in a binary compound as more metallic and the other as less metallic, or more non-metallic, it is useful to be able to represent this distinction in less cumbersome terms. This we do by calling one constituent positive and the other negative. The choice of which to consider positive, instead of being entirely arbitrary, is made to conform to the behavior of the compounds in so far as they may be decomposed by an electric current. When an electric current is passed through a solution of a binary compound, or through the liquid formed by its fusion, it may often be shown that the more metallic constituent travels with the positive current and may often be discharged as the free element at the cathode, or negative pole, while the non-metallic constituent may travel with the negative current, and may often be discharged at the anode, or positive pole. Accordingly, it is customary to refer to the metallic constituent as the positive element in the compound, and to the other as the negative element. Thus, when a water

solution of hydrogen chloride gas is electrolyzed, using electrodes which are not acted upon chemically, such as graphite or platinum, hydrogen gas is liberated at the negative pole, whence it is considered the positive or metallic element, while chlorine gas is liberated at the positive pole, so it is considered the negative element. Similarly, aluminum oxide may be dissolved in certain fused salts and decomposed by an electric current, giving aluminum, the positive element, at the negative pole, and oxygen, the negative or non-metallic element, at the positive pole.

In writing formulas of compounds the usual practice is to put first the symbol of the metallic or positive element, *e.g.*, $CuCl_2$, H_2O, NaCl, PbS, S_2Cl_2. Sometimes the same element may be the more negative element in one compound and the more positive in another as is apparently the case, respectively, with sulfur in the two compounds just given. Unfortunately this convention is transgressed in a few cases like that of ammonia, usually written NH_3, where the convention would require H_3N.

It is interesting to note that where more than one compound of the same element exists, the physical characteristics of the compounds seem to approach those of the element which is in excess. For example, there are a number of sulfides of sodium and potassium. Those containing least sulfur, as K_2S, are white in color, but the color becomes increasingly yellow as more sulfur is present, and the higher sulfides act chemically very much like pure sulfur. Again, where more than one chloride of a metal exists, as illustrated by $SnCl_2$ and $SnCl_4$, $FeCl_2$ and $FeCl_3$, $PbCl_2$ and $PbCl_4$, the one containing more chlorine is more volatile, which we may connect with the fact that chlorine is a gas.

Oxides and Sulfides. Among the most important of all chemical compounds are the oxides, largely because we live in an atmosphere containing oxygen, so that there is great opportunity for oxides to form. All the elements form oxides, except fluorine and the rare gases of the atmosphere, argon, neon, etc. Most of these oxides may be formed directly by burning the elements in the air, and this process, especially when light and heat are involved, is called combustion. Most fuels consist of carbon or hydrogen or their compounds. Coke and anthracite coal are fairly pure carbon, and burn to give carbon monoxide, CO, when the supply of air is insufficient, and to form carbon dioxide, CO_2, when the air supply is sufficient. Other fuels, like gas, kerosene, gasoline and wood, contain either hydrogen or compounds of hydrogen with carbon, and, in the case of wood, oxygen as well. In all of these cases we have the oxidation of the hydrogen, on burning to form water, along with the formation of CO_2.

Certain metals, called the base metals, oxidize quite readily. Sodium burns easily in air. Magnesium, when powdered, is an exceedingly combustible substance, giving off a very bright light, which makes it a useful constituent of flash-powders. We are accustomed to think of metals like zinc and aluminum as incombustible, but that is because the solid oxides formed, unlike the gaseous oxides of carbon, hydrogen, sulfur, etc., coat the metal, preventing access of the oxygen to the atter. If these metals are finely divided, as in turnings, foil or powder, they burn quite readily. A still less positive metal, like iron, will not burn by itself in the air, but when in the form of wire will burn vigorously in pure oxygen and will rust in moist air forming an iron oxide, by a process similar to ordinary com-

bustion. A nobler metal like copper cannot be ignited, even in pure oxygen, but if it is kept sufficiently hot by holding it in an ordinary flame, it will gradually change to oxide. The noblest metals, like silver, gold and platinum, will not combine with oxygen directly. Their oxides must be prepared by roundabout means, and are easily decomposed. They are the metals which occur free in Nature.

Sulfur is an element which is capable of forming several types of compounds, as we shall see later, but we may note now that in one of these types it closely resembles oxygen. Accordingly we have sulfides analogous to oxides in nearly all cases. The following formulas may be given to show this resemblance:

H_2O, Cu_2O, CuO, ZnO, Al_2O_3, CO_2, SnO, SnO_2, Ag_2O, Na_2O_2,
H_2S, Cu_2S, CuS, ZnS, Al_2S_3, CS_2, SnS, SnS_2, Ag_2S, Na_2S_2.

Nearly all the oxides and sulfides of the metals are insoluble in water and have very high melting points.

Halides. Next to the oxides, the halides of the metals are probably most important By this name we designate the binary compounds of the elements known as the halogens, *i.e.*, fluorine, chlorine, bromine and iodine. (The name comes from the Greek for sea-salt, sodium chloride being typical of the group.) The halides of a given metal are usually all very much alike as to solubility, appearance, etc. Those of fluorine show the least resemblance to the others. Nearly all of them are easily dissolved by water, and most of them can be melted without decomposition at moderate temperatures.

The Relation of the Relatively Positive and Negative Characters of Elements to the Reactions of Their Compounds.

(*a*) **Displacement.** The fruitfulness of the conception of the relatively positive and negative characters of the elements is illustrated by its application in helping to determine the course of reactions. We may consider, first, reactions in which one element displaces another. What has been said regarding the relation between the stability of compounds and the positive and negative character of their component elements would lead us to expect that a more positive element would replace a less positive one in a compound. This is usually the case, as illustrated by the following reactions:

$$3\,Na + AlCl_3 = 3\,NaCl + Al,$$
$$Fe + CuCl_2 = FeCl_2 + Cu,$$
$$Cu + HgCl_2 = CuCl_2 + Hg.$$

Similarly, a more negative element may replace a less negative one, as illustrated by the reaction

$$CaI_2 + Cl_2 = CaCl_2 + I_2.$$

Carbon has a much greater power to combine with oxygen than would be inferred from its non-metallic character, and does not lend itself to inclusion in the arrangement previously given. We may, however, compare the relative stability of various metallic oxides by considering the relative ease with which they may be reduced to metal by carbon. Aluminum oxide, Al_2O_3, for example, is so stable that carbon is unable to remove the oxygen from it. The oxide of zinc, a less positive metal, can be so reduced, the zinc of commerce being obtained in this way.

$$ZnO + C = Zn + CO.$$

The oxides of iron, a still less positive metal, can be reduced more easily.

$$Fe_2O_3 + 3\,C = 3\,CO + 2\,Fe.$$

The dioxide of tin is still more easily reduced, as tin is nobler than iron.

$$SnO_2 + 2\,C = Sn + 2\,CO.$$

(*b*) **Metathesis.** When two compounds are brought together there occurs frequently a type of reaction known as a **metathetical** reaction, in which certain elements or groups of elements change places. The following equations represent reactions of this type:

$$AgCl + KI = AgI + KCl.$$
$$CaO + 2\,HCl = CaCl_2 + H_2O.$$
$$Al_2S_3 + 3\,H_2O = Al_2O_3 + 3\,H_2S.$$

The important thing to note is that the more metallic element of one compound changes place with the more metallic element of the other. (In each case the positive element is written first in the formula, according to the convention stated previously.) We seldom find such a reaction as

$$AgCl + KI = AgK + ClI$$

(which would represent the formation of compounds containing like elements) when unlike elements have the opportunity to combine, as represented above. Of course, it may not be possible to tell whether the most stable pair of compounds would be silver chloride and potassium iodide or silver iodide and potassium chloride. This would have to be determined by experiment, or by the aid of criteria to be discussed in Chapters XII and XIII.

(*c*) **Addition.** Another type of reaction between binary compounds occurring frequently where the two compounds have one element in common, consists simply of a combination to form a less simple type of compound. The most interesting of these combinations are those taking place between oxides. In order to understand these combinations, we may regard the oxides as possessing a residual positive or negative nature dependent on the character and the amounts of the elements in the oxide. Thus, the more positive elements would yield more positive oxides, and vice versa, and also, where two oxides of the same element exist, the one containing more of the highly negative element, oxygen, would be more negative. To illustrate, we give a list of oxides arranged according to these ideas, with the more positive oxides at the top, an arrangement similar to that we used before when considering the elements.

K_2O, Na_2O
CaO, MgO
Al_2O_3, ZnO
H_2O
CO_2
SO_2
SO_3

In accordance with this arrangement, and its governing idea, we find that the oxides far apart show great tendency towards combination. Plaster of Paris, which may be considered as a compound of CaO and SO_3, is a very stable substance. Limestone, $CaO \cdot CO_2$ (usually written $CaCO_3$), is less stable, and is broken down at a red heat into the gas CO_2 and quicklime, CaO. When water, H_2O, is added to

quicklime, slaked lime is formed, $CaO \cdot H_2O$ (also written $Ca(OH)_2$), and this, on heating, is broken down (into quicklime and steam) more easily than is limestone. The combination between H_2O and the oxide of a still more positive metal than calcium gives, as we should expect, a more stable compound than $Ca(OH)_2$. Illustrations might be multiplied ad libitum. Enough has been said to show what oxides might be expected to combine most readily, and to show how compounds of this sort might be classified according to the oxides of which we may consider them to be composed.

As might be expected from the similarity of sulfur and oxygen compounds, many double sulfides exist, similar to the compounds between the oxides just discussed. These are numerous in the mineral world, as exemplified by $3\ Cu_2S \cdot Sb_2S_3$, $PbS \cdot Sb_2S_3$, $3\ Ag_2S \cdot As_2S_3$.

Many combinations of halides exist corresponding to those of oxides, though they are not so numerous or important. The chlorides of the base metals and those of the noble metals fulfill our expectations in furnishing compounds of this nature, some of which, like $KCl \cdot AuCl_3$, $2\ KCl \cdot PtCl_4$, are very stable. With iodides we have, similarly, $2\ KI \cdot HgI_2$, etc. The fluorides are especially prone to form double compounds, as witnessed by $HF \cdot KF$, $2\ HF \cdot SiF_4$, $BaF_2 \cdot SiF_4$.

Classification of Compounds. We have seen that binary compounds may be classified very simply according to the positive and negative elements of which they are composed. In this sense we might investigate and compare the various silver compounds and their reactions, on the one hand, or the various chlorides, on the other hand. When we come to compounds containing more than two elements we have seen, farther, how we may classify them according to the

oxides, chlorides, sulfides, fluorides, etc., of which we may consider them composed. For many purposes this is a most useful classification. There is, however, another way in which we may regard their constitution, a way especially useful for reactions occurring in water solution.

We have seen how a compound like silver sulfate, Ag_2SO_4, may be regarded as composed of the oxides Ag_2O and SO_3, as is indicated by writing the formula $Ag_2O \cdot SO_3$. Many of its reactions could profitably be represented in this way. However, if we mix a solution of this compound with one of potassium chloride, KCl, instead of an interchange of K and Ag_2O, we have an interchange of K and Ag, represented by the equation:

$$2\,KCl + Ag_2SO_4 = K_2SO_4 + 2\,AgCl.$$

It would evidently be more satisfactory, in this reaction, to regard silver sulfate as composed of Ag and SO_4. This group, SO_4, is called the **sulfate radical**. In the reaction between calcium sulfate, $CaSO_4$, and sodium carbonate, Na_2CO_3, we might still use the oxide notation, writing:

$$CaO \cdot SO_3 + Na_2O \cdot CO_2 = CaO \cdot CO_2 + Na_2O \cdot SO_3.$$

Or, we might consider the reaction to be an interchange of metals rather than an interchange of oxides, writing:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

When, however, we use calcium chloride, $CaCl_2$, instead of $CaSO_4$, an interchange of metals represents the only type of reaction possible, so that we must write

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\,NaCl.$$

From this and other examples that might be given, we see that the second method of considering the constitution of

these compounds is much more inclusive, besides allowing us to consider both types of compounds as made up of the same fundamental constituents. The same applies to other double compounds, such as chlorides, as well as to oxides. If we mix solutions of Na_2PtCl_6 and K_2SO_4, the reaction is:

$$Na_2PtCl_6 + K_2SO_4 = K_2PtCl_6 + Na_2SO_4,$$

implying that the reaction represents an interchange between sodium and potassium and the **radicals** $PtCl_6$ and SO_4. If the constitution of the new compounds were that represented by $2\,NaCl \cdot PtCl_4$ and $K_2O \cdot SO_3$, we should be led to expect the wrong type of interchange entirely. Our conclusion must be that for some reactions one point of view is more useful, and for other reactions the other is better. Thus, when dealing with the decomposition of calcium carbonate by heat it is useful to think of it as a compound of CaO and CO_2, whereas its reactions in the presence of water correspond better with the idea that it is composed of calcium and the carbonate radical. Corresponding to this latter conception we would classify compounds according to the constituent elements or radicals which take part in metathetical or interchange reactions. We will proceed to do this so as to point out three very important types, *i.e.*, acids, bases and salts.

We have seen that it is usually better not to attempt to distinguish between compounds such as KCl and K_2O, K_2S, etc., but to consider them all as compounds of potassium, from which standpoint we would investigate the common properties of potassium compounds. Similarly we might investigate in groups, calcium compounds, lead compounds and those of all the positive elements or metals. Then, in

grouping the negative constituents, we would have, in addition to single elements, like chlorine, etc., negative groups, or radicals, containing more than one element, like sulfate radical, SO_4, carbonate radical, CO_3, nitrate radical, NO_3, etc., and we would seek to determine what properties were common to all sulfates, carbonates and nitrates, respectively. (It is seldom that the positive constituent consists of more than a single metallic element.) The first of these classes for us to investigate is that composed of compounds in which the positive element is hydrogen.

Acids. The most obvious property of many compounds in which hydrogen is the positive constituent is a sour taste. This taste we are accustomed, in everyday life, to ascribe to substances we call acids, and since only certain hydrogen compounds give such a taste, we may consider it the property of this kind of combined hydrogen. There are a number of more or less familiar acids which we may recall and characterize briefly. Hydrochloric acid, HCl, is a gas when in the pure state, but it is very soluble in water, forming the solution sometimes known as "muriatic acid." Sulfuric acid, H_2SO_4, in the absence of water, is a dense syrupy liquid, and has the common name of "oil of vitriol." It is manufactured and used in larger quantities than any other substance for purely chemical purposes. Nitric acid, HNO_3, is a fuming corrosive liquid extensively used to dissolve the nobler metals and in the manufacture of explosives. Acetic acid, $HC_2H_3O_2$ (only one of the hydrogen atoms of which has acid properties), is the acid of vinegar. Phosphoric acid, H_3PO_4, is used in the phosphate drinks at the soda fountain. Boric acid, H_3BO_3, or "boracic acid," is a solid giving a solution of very faintly acid properties. It finds use as a mild

antiseptic. Oxalic acid, $H_2C_2O_4$, a solid in the pure state, finds frequent use as a chemical reagent. The various fruit juices contain characteristic acids, such as citric acid, found in lemons, tartaric acid in grapes, malic acid in apples, etc.

Whenever we have the sour taste of an acid we may notice certain other properties which are, therefore, likewise characteristic of acids. The hydrogen of an acid may be replaced by a metal, indirectly when using a suitable compound of the metal, as we shall see later when discussing bases, and directly when using the free metal, if the acid is not too weak and if the metal is a base one, such as zinc or magnesium. Ordinary acids, then, if not too weak, will dissolve base metals like zinc. The following equation represents a typical reaction, zinc and sulfuric acid forming zinc sulfate and hydrogen gas:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Again, unless an acid is extremely weak in its acid properties, when it is brought in contact with a carbonate, such as sodium carbonate, Na_2CO_3, "washing soda," it liberates the weak carbonic acid, H_2CO_3, which breaks down into water and carbon dioxide gas, producing an effervescence unless a great deal of water is present. To illustrate this, we may give the equation for the action of sulfuric acid on sodium carbonate:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2.$$

One of the most useful ways of detecting acids, especially when they are very dilute, is by means of certain natural and artificial coloring matters called **indicators**, because they indicate whether or not a solution is acid. Among

these may be mentioned litmus, a plant extract giving a blue color in pure water which is changed to red by the minutest traces of acid. Another indicator, an artificial dye called methyl orange, gives a yellow solution in water, changing to orange and then to red as acid is added. It takes more acid in a given amount of water to change the color of this indicator than it does to turn litmus red. Another, methyl violet, requires a still more concentrated acid to change it successively from violet, through blue, green and yellow as more acid is added.

Bases. There is another class of compounds which are capable of neutralizing or destroying the above properties shown by acids in water solution. These are all characterized by the radical OH, called hydroxyl, and are compounds of this group with metals. They are called bases. Most of them are insoluble in water, or nearly so, the chief exceptions being sodium hydroxide, NaOH, sometimes called "caustic soda," potassium hydroxide, KOH, sometimes called "caustic potash," the solution of which is known often as "lye," and barium hydroxide, $Ba(OH)_2$. Calcium hydroxide, $Ca(OH)_2$, "slaked lime," is sparingly soluble; its solution is known as "lime water." To these should be added ammonium hydroxide, NH_4OH, formed when ammonia gas, NH_3, is dissolved in water. The group NH_4 acts like a metal in combination. The soluble bases, especially the first two, are often called **alkalis**, and their solutions **alkaline**. The property fundamental to bases is their ability to neutralize acids. This reaction is an exchange such that the hydrogen of the acid and the hydroxyl of the base unite to form water. The equations representing neutralization are among the easiest to write, for we need

one OH group for every hydrogen atom. The following equations show examples of neutralization:

$$NaOH + HCl = HOH \text{ (or } H_2O) + NaCl,$$
$$2\,KOH + H_2SO_4 = 2\,H_2O + K_2SO_4,$$
$$Ca(OH)_2 + 2\,HNO_3 = 2\,H_2O + Ca(NO_3)_2,$$
$$Al(OH)_3 + 3\,HCl = 3\,H_2O + AlCl_3,$$
$$2\,Al(OH)_3 + 3\,H_2SO_4 = 6\,H_2O + Al_2(SO_4)_3.$$

Besides the ability to neutralize acids, and their common constitution as hydroxides of metals, which characterize all bases, there are certain additional important qualities of the solutions of **soluble bases, or alkalis**, which we may regard as the properties of the hydroxyl radical dissolved in water. One of these is a peculiar taste, for which we have no word so descriptive as is the word "sour" for the corresponding taste of acids. It is the taste of lime water. Again, alkaline solutions have an emulsifying action on fats, and a tendency to produce soap with grease, which gives a soapy feeling when such a solution is rubbed between the fingers. Most conclusive, however, are the colors given to indicators. When litmus has been turned red by acid the addition of alkali will restore the blue color. Similar changes are produced with the other indicators previously mentioned. A very useful indicator is phenolphthalein, which is colorless in pure water or in acid, but is turned a deep red by very dilute alkali. Still others, such as trinitrobenzene, require considerable amounts of alkali in order to produce a change in color. By a suitable choice of indicators it is possible to cover the entire range from strongly acid solutions, through neutral, to strongly alkaline solutions.

Salts. The result of the neutralization of acids and bases is the formation of water, together with a substance called a **salt**. The name is derived from the typical substance common salt, sodium chloride, and salts in general, like it, are usually solid crystalline substances at ordinary temperatures. The number of salts known is nearly equal to the product of the number of existing positive constituents of bases and the number of negative constituents of acids. The natural classification of all salts is according to these constituents or radicals. Thus, we might make a study of all the salts of zinc, on the one hand, or of all sulfates, on the other. In a sense the acids are simply the salts of hydrogen, and the bases those of hydroxyl; the extremely important rôle played by acids and bases, however, justifies their separate classification. We see that the idea of a salt is a more general one than is the idea that a substance may be made up of positive and negative oxides or halides, etc., for it includes all substances which contain decidedly positive and negative constituents. The question as to how positive and negative these constituents must be in order that the compound may be considered a salt is no more capable of an arbitrary answer than is the question as to how sour a solution of a substance must be in order that the substance may be called acid. We have all gradations between undoubted salts, like common salt, through substances of feeble salt-like nature, such as tetrachloride of tin, to sulfur or iodine chlorides, which are not usually considered as salts at all. Sharp boundaries of any sort are not very frequent in Nature, and we must always remember that many of our classifications are purely for the sake of convenience and not to be overworked. We may make definitions of such

terms as metal, salt, acid, etc., but when we come to fit actual substances to our definitions, we are confronted by such problems as how good a conductor, or how malleable, etc., an element must be to be called a metal, or again, how much difference there must be in the positive and negative character of the elements in a compound before we will be willing to class it as a salt. History shows much waste of paper and good temper by futile controversies of this sort.

Anhydrides of Acids and Bases. From what has been said above it is evident that a base may be looked upon either as a compound of a metallic element with the hydroxyl radical, or as a compound of a metallic oxide with water. Several further examples may be given in the following equations:

$$Na_2O + H_2O = 2\,NaOH,$$
$$CaO + H_2O = Ca(OH)_2,$$
$$Cu(OH)_2 = CuO + H_2O,$$
$$2\,Al(OH)_3 = Al_2O_3 + 3\,H_2O.$$

On the basis of this relation between the hydroxides and the oxides the latter are often called **basic anhydrides**, the latter word signifying the removal of water. Similarly, acids which contain oxygen as well as hydrogen may be dehydrated by the removal of water, or may be formed from the non-metallic oxide and water, as the case may be. The following will serve as examples:

$$H_2O + CO_2 = H_2CO_3,$$
$$H_2O + N_2O_5 = 2\,HNO_3,$$
$$H_2O + SO_2 = H_2SO_3,$$
$$H_2O + SO_3 = H_2SO_4,$$
$$H_2O + P_2O_5 = 2\,HPO_3,$$
$$2\,H_2O + P_2O_5 = H_4P_2O_7,$$
$$3\,H_2O + P_2O_5 = 2\,H_3PO_4.$$

The oxides from which acids may be formed are likewise often called **acid anhydrides**. The important thing to note is the similarity of the chemical behavior of the acid and basic anhydrides to that of their respective acids and bases. When acids and bases neutralize each other they produce a salt and water. Since the difference between the acid or base and its anhydride is simply water, the difference between their reactions with each other and ordinary neutralization is simply in the amount of water produced. We may write a series of equations to illustrate this relationship:

$$Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2\,H_2O,$$
$$CaO + H_2SO_3 = CaSO_3 + H_2O,$$
$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O,$$
$$CaO + SO_2 = CaSO_3.$$

We see here the fusion of the two ideas of the classification of a salt like $CaSO_3$ either as composed of a positive metal and a negative acid radical, or else as a compound of a positive and relatively negative oxide. We see also that a metallic oxide will neutralize an acid, or an acid anhydride will neutralize a base, hence we must expect the chemistry of the anhydrides and of their acids and bases to be very similar.

EXERCISES

1. Make a list of the characteristics of acids and bases.

2. What is meant by each of the terms, alkali, alkaline reaction, radical, metathesis, neutralization, anhydride?

3. Determine, by subtracting H_2O in proper proportion, what are the anhydrides of the following substances: HNO_3, H_2CO_3, $Fe(OH)_3$, $Fe(OH)_2$, H_3PO_4, HPO_3, H_3PO_3, $CuOH$, H_2SO_3.

4. From your knowledge of the metallic or non-metallic nature of the elements involved, state which constituents of the following

pairs of compounds might be expected to exchange if they react with each other: (1) Ag_2SO_4 and Na_2CO_3; (2) $CuCl_2$ and K_2S; (3) ZnS and 2 HCl; (4) $Ca(OH)_2$ and Na_2CO_3; (5) $Ca(OH)_2$ and H_2SO_4.

5. Which substance in each of the following pairs would decompose more easily, on heating, in the manner represented by the respective equations:

(1) $CuCO_3 = CuO + CO_2$ or
$CaCO_3 = CaO + CO_2$;

(2) $CuCO_3 = CuO + CO_2$ or
$CuSO_4 = CuO + SO_3$;

(3) $Ca(OH)_2 = CaO + H_2O$ or
$2Al(OH)_3 = Al_2O_3 + 3H_2O$?

CHAPTER VI

VALENCE. WRITING EQUATIONS

For the purpose of writing formulas and equations it is very important to know the number of atoms of substances that are likely to combine to form compounds, without being under the necessity of performing an analysis of each substance or of remembering its composition as an isolated fact. It is possible to do this by the aid of a number, or numbers, characteristic of each element, which indicate rather uniformly the relative number of atoms of the different elements that may be found in a molecule. The number expressing this combining value for an element is called its **valence**. We shall first see how the valence of an element may be determined and then see how it may be used in predicting formulas and writing equations.

Assignment of Valence Numbers. If we classify the binary compounds of hydrogen according to the numbers of atoms of hydrogen per atom of the other element, we will find them dividing into groups as follows:

HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si
HI		H_3As	

We notice that the elements of these compounds may be divided according to their power to combine with hydrogen. Elements of one group, *e.g.*, Cl, Br, I, are able to combine atom for atom with hydrogen; those of another, repre-

sented by O and S, have atoms which can combine with two atoms of hydrogen; in still another group the atoms can combine each with three hydrogen atoms, and in another with four. Evidently the elements in the second, third and fourth columns have respectively 2, 3 and 4 times the combining power, measured with hydrogen, that the elements in the first group have. Moreover, we do not find elements having a smaller combining power than hydrogen. We may thus take the hydrogen atom as our unit for determining the combining value or valence. We will find, then, that we are able to measure the combining value, or valence, of any kind of atom by determining from the formulas of some of its compounds its power either to combine with hydrogen or to replace it in some compound such as those given in the table. Thus an atom of oxygen, O, can combine with two atoms of hydrogen, as in H_2O, while an atom of calcium, Ca, can replace two atoms of hydrogen, as is seen by comparing CaO with H_2O. It is, however, important to distinguish between power to combine with hydrogen and power to replace hydrogen, for atoms that can replace hydrogen can replace each other, but as a rule cannot combine with each other, while atoms that can combine with hydrogen can also replace each other but cannot as a rule combine with each other. Calcium and oxygen are both related to two atoms of hydrogen, but in a different way, the former replacing hydrogen, the latter combining with two atoms of hydrogen. We must, therefore, distinguish between two kinds of valence, as well as between different numerical values. This we will do by calling one positive and the other negative. The decision as to which shall be positive is based on the electrical be-

havior, to be explained more fully in Chapter X, and follows the metallic or non-metallic character of the elements discussed in Chapter V, where we called the more metallic element in the compound the positive element, and vice versa. In the above compounds the hydrogen appears to be the positive constituent, so that we will call its valence + 1. Any element, furthermore, which replaces hydrogen will be considered as showing a positive valence, while any element combining with hydrogen or its equivalent will be considered as showing negative valence.

Accordingly, in the above list of compounds, the valence of Cl, Br and I is considered − 1, that of O and S, − 2, that of N, P and As, − 3. In CaO the valence of Ca is + 2, since that of O is taken as − 2, also since it appears, in comparing H_2O and CaO, that one atom of calcium replaces two of hydrogen. In NaCl the valence of Na is + 1 and that of Cl, − 1, as can be seen by comparing NaCl with HCl, from which it may be obtained. In Al_2O_3 the valence of Al is 3, because the valence of oxygen is − 2 and three atoms represent − 6, hence the two atoms of aluminum represent + 6, each atom being + 3. As further illustrations we may give a number of compounds, writing under each element the valence per atom, and indicating the multiple of this corresponding to the number of atoms in the molecule. The sum of the total positive and negative valence is, of course, zero.

$MgCl_2$	$SnCl_4$	H_3BO_3
+ 2, 2(−1)	+ 4, 4(−1)	3(+ 1), + 3, 3(− 2)
NaOH	Na_2S	PbO_2
+ 1, − 2, + 1	2(+ 1), − 2	+ 4, 2(− 2)

It is possible to consider the valence of the radicals discussed in Chapter V, without paying any attention to the valence of the atoms within the radical. In H_2SO_4 it is obvious that the valence of the SO_4 radical is -2, and in K_2PtCl_6 that the valence of the $PtCl_6$ radical is -2. We may, similarly, speak of the valence of the hydroxyl radical as -1, of that of the $Fe(CN)_6$ radical in $K_4Fe(CN)_6$ as -4. Where the radical in question remains intact in a reaction, it is unnecessary to consider the valence of its component elements.

Elements Exhibiting More Than One Valence. Many of the elements show more than one valence in their various compounds. Tin, for example, gives two series of compounds, the stannous compounds, in which the valence of tin is 2, and the stannic compounds, in which it is 4, as exemplified by the following:

Stannous

$SnCl_2$	SnO	SnS	$Sn(OH)_2$
$+2, 2(-1)$	$+2, -2$	$+2, -2$	$+2, 2(-2, +1)$

Stannic

$SnCl_4$	SnO_2	SnS_2	$Sn(OH)_4$
$+4, 4(-1)$	$+4, 2(-2)$	$+4, 2(-2)$	$+4, 4(-2, +1)$

In this case we have no doubt that the tin is the element that changes valence rather than the other elements present in the above compound, because the other elements react in the same way in both cases. For example, upon the addition of silver nitrate solution to a solution of either of the chlorides of tin the same silver chloride precipitate is produced. We must, therefore, have the same kind of chlorine in both compounds. Again, both sulfides give

hydrogen sulfide when acted upon by hydrochloric acid, as represented by the equations:

$$SnS + 2\,HCl = SnCl_2 + H_2S,$$
$$SnS_2 + 4\,HCl = SnCl_4 + 2\,H_2S.$$

As contrasted with the tin compounds we have two oxides of barium, BaO and BaO_2. These appear analogous to the oxides of tin just mentioned, and we might be inclined to say that there must be two series of barium compounds in which barium would have valences of 2 and 4 respectively. However, we fail to find any other barium compounds in which the valence appears to be other than 2. Also, on investigating the chemical reactions of BaO_2 we find that while it reacts to give barium compounds in which the valence of barium is evidently 2, it gives oxygen compounds quite different from the ordinary oxygen compounds. The following equations will bring out this contrast in the behaviors of SnO_2 and BaO_2:

$$SnO_2 + 4\,HCl = SnCl_4 + 2\,H_2O,$$
$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

There are no other barium compounds and no other hydrogen compounds in which we would be tempted to assign to those elements any but the ordinary valences, 2 and 1 respectively. We find by experiment, however, that the oxygen in these compounds, together with a few others, cannot be classed with the oxygen in most compounds. It behaves quite differently, and it is therefore logical to ascribe to it a different valence. We therefore conclude that the 2 atoms of oxygen in these compounds have together a valence of -2. It is impossible to decide whether these two atoms

have both the same valence, − 1, or different valences, like 0 and − 2, whose mean is − 1. For practical purposes, however, it is unnecessary to distinguish these atoms from each other, so that we may consider them both as having a valence of − 1. In all other oxygen compounds it is satisfactory to ascribe to the oxygen a valence of − 2.

A similar difficulty is encountered with respect to the valence of sulfur in sodium thiosulfate, $Na_2S_2O_3$, the " hypo " of the photographer. Since Na and O have valences respectively of 1 and − 2, as usual, that of the two sulfur atoms together must be + 4. This does not necessarily mean, however, that both of these atoms have the same valence, 2, for a total of 4 would be obtained if one valence were 3 and the other 1, or if one were 5 and the other − 1, etc. The probable valence, again, can be determined with any degree of certainty only by finding what kinds of compounds the two atoms of sulfur produce when thiosulfates are decomposed.

Some of the elements, especially some of the non-metals, exhibit even more than two valences. In the following compounds, KCl, KClO, $KClO_2$, $KClO_3$ and $KClO_4$, the potassium and the oxygen are believed to have the usual valences, 1 and − 2, respectively, which indicates that the valences of the chlorine are respectively − 1, + 1, 3, 5 and 7. Likewise with phosphorus we have such compounds as H_3P (usually written PH_3, though the hydrogen is doubtless the positive element), H_3PO_2, H_3PO_3 and H_3PO_4. In these compounds the valences of phosphorus seem to be respectively − 3, + 1, 3 and 5.

Use of Valence in Classifying Compounds. Where an element shows a varying valence, as in the instances just

given, the determination of the valence gives a means of classifying together those compounds in which the element has the same valence, so that we may be led to anticipate similarities in chemical behavior within the same class of compounds. In the compound $NaPO_3$, which has no clear connection with any of the other compounds above, a simple calculation shows that the phosphorus has a valence of 5, wherefore it is to be classed with H_3PO_4. The same applies to an apparently different compound, $Mg_2P_2O_7$ (cf. $MgCl_2$). On the other hand, in the compound $Na_4P_2O_5$, the valence of the phosphorus places it with H_3PO_3. A proper understanding of the reactions of these different classes of compounds is aided by considering valence. Thus PCl_3, where the valence is 3, yields H_3PO_3 with water, while PCl_5 yields H_3PO_4. Again, a regard for valence makes it evident that neither P_2O_3 or P_2O_5, in reacting with water, could be expected to give a compound such as H_2PO_3.

Writing Formulas with the Aid of Valence. It has just been shown that the valences of the elements can be determined by examining a few of the compounds of each element. Having done this, it is possible to predict the formulas of other compounds. In the table below are given valences of positive and negative constituents of compounds as determined on the previous pages, together with the formulas of the compounds that might be expected to result from their combination.

In this table we have given a large number of compounds not previously considered, solely on the basis of valences deduced from the few that have been considered. Illustrations might, of course, be multiplied indefinitely.

Constituent		Cl	Br	OH	O	S	SO_4	PO_4
Valence		− 1	− 1	− 1	− 2	− 2	− 2	− 3
H	1	HCl	HBr	HOH	H_2O	H_2S	H_2SO_4	H_3PO_4
Na	1	NaCl	NaBr	NaOH	Na_2O	Na_2S	Na_2SO_4	Na_3PO_4
K	1	KCl	KBr	KOH	K_2O	K_2S	K_2SO_4	K_3PO_4
Ca	2	$CaCl_2$	$CaBr_2$	$Ca(OH)_2$	CaO	CaS	$CaSO_4$	$Ca_3(PO_4)_2$
Ba	2	$BaCl_2$	$BaBr_2$	$Ba(OH)_2$	BaO	BaS	$BaSO_4$	$Ba_3(PO_4)_2$
Al	3	$AlCl_3$	$AlBr_3$	$Al(OH)_3$	Al_2O_3	Al_2S_3	$Al_2(SO_4)_3$	$AlPO_4$
Sn	2	$SnCl_2$	$SnBr_2$	$Sn(OH)_2$	SnO	SnS	$SnSO_4$	$Sn_3(PO_4)_2$
Sn	4	$SnCl_4$	$SnBr_4$	$Sn(OH)_4$	SnO_2	SnS_2	$Sn(SO_4)_2$	$Sn_3(PO_4)_4$

Writing Equations. In connection with chemical equations it is important to realize that the mere writing of the equation confers no obligation upon the substance involved to behave as indicated by the equation. The obligation is rather upon the one who writes the equation to endeavor to make it correspond to an actual or possible reality. A complete justification of an equation would require the experimental determination both of the substances produced, their formulas and their relative amounts. To avoid this labor and to aid in predicting possible reactions we may avail ourselves of the results of other experimenters which enable us to determine valence. We may expect that where a reaction takes place at all it will tend to produce compounds between elements or radicals having valence of different signs, and also in the proportions demanded by the numerical magnitude of the valences. It then becomes necessary to take the proper number of molecules of each substance so that there will be the same total number of atoms of each element on both sides of the equation, since it is this equality that justifies our use of the term "equation." These steps will be best illustrated by examples.

Let us consider, first, the reaction between aluminum and Fe_3O_4 to form aluminum oxide and iron. To be absolutely

certain of the formula of the aluminum oxide produced we would have to determine it by analysis. We do not, however, find aluminum compounds in which the valence of aluminum is other than 3, as we see it in $AlCl_3$. This would lead us to anticipate that the oxide formed would be Al_2O_3, which is correct. Accordingly, we have Al and Fe_3O_4 giving Al_2O_3 and Fe. We must next adjust the number of molecules so that there will be the same number of atoms of each element on each side of the equation. It is obvious that we must take 3 Fe_3O_4 to get an integral number, 4, of Al_2O_3 molecules. Adjusting the number of atoms of Al and Fe, we have as the equation,

$$3\ Fe_3O_4 + 8\ Al = 9\ Fe + 4\ Al_2O_3.$$

It is always desirable to check the equation written by comparing the number of atoms of each element on each side of the equation. They should, of course, be equal.

The products of the reaction between solutions of $BaCl_2$ and $Al_2(SO_4)_3$ would evidently be those formed by an interchange of the positive constituents, to form aluminum chloride and barium sulfate. From the valences of the four constituent elements and radicals we would predict the formulas of the latter to be $AlCl_3$ and $BaSO_4$. Our equation is therefore, in part,

$$BaCl_2 + Al_2(SO_4)_3 = BaSO_4 + AlCl_3.$$

Adjusting the number of molecules of each substance so as to make the equation balance, we have finally,

$$3\ BaCl_2 + Al_2(SO_4)_3 = 3\ BaSO_4 + 2\ AlCl_3.$$

When solutions of $Fe(NO_3)_3$ and $Ba(OH)_2$ are mixed a precipitate is produced such as we might expect would be

formed by the interchange of the constituents of the same sign, *i.e.*, Fe and Ba. The valence of the Fe in this compound is seen to be 3 if we compare it with HNO_3. The valence of each of the other constituents we have already learned from the previous pages, so that the formulas of the compounds produced might be predicted as $Fe(OH)_3$ and $Ba(NO_3)_2$. Adjusting the number of molecules of these four substances so as to represent no gain or loss of atoms, we write as the equation,

$$2\ Fe(NO_3)_3 + 3\ Ba(OH)_2 = 2\ Fe(OH)_3 + 3\ Ba(NO_3)_2.$$

Equations for the neutralization of acids and bases are very easily written by regarding the union of one H of the acid with one OH of the base. The numbers of molecules of acid and base must therefore be such that they will yield equal numbers of these constituents of water. Examples of neutralization equations illustrating this may be found on page 79.

Oxidation and Reduction. We have certain reactions in which there is a change of valence on the part of two or more elements. In both of the following reactions,

$$2\ SnO + O_2 = 2\ SnO_2 \text{ and}$$
$$SnCl_2 + Cl_2 = SnCl_4$$

the tin increases in valence, going from a compound of one class to that of another, a different reaction from those illustrated on page 88. In the first we have the addition of oxygen to the tin, wherefore we say that the tin has undergone **oxidation.** In the second, though no oxygen is involved, the same change of valence on the part of the tin takes place, so that the same name is applied to the pro-

cess. **The term oxidation is applied whenever valence takes on a more positive (or less negative) value.** The opposite process, the removal of oxygen or, in general, the decrease in valence, is called by the more obviously general name **reduction.** In the two following equations, starting with metallic tin, we evidently have oxidation of the tin likewise:

$$Sn + Cl_2 = SnCl_2,$$
$$2\,Sn + O_2 = 2\,SnO.$$

In order to make this accord with our definition the valence of metallic tin must be zero. It is important to remember this throughout in dealing with the free elements. When we speak of the valence of an element we must refer to its valence in a particular compound or class of compounds. Accordingly, the oxygen and chlorine in the above equations are both reduced.

In balancing equations involving oxidation and reduction the principle invoked is to make the total increase in valence of all the atoms oxidized equal to the total decrease in valence of all the atoms reduced. Further discussion of this type of equation will be resumed later in Chapter XV.

EXERCISES

1. What is the probable valence of each radical and element in each of the following compounds: $CuSO_4$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $PbCO_3$, $CrCl_3$, MgO, NH_4Cl, CuS, $FeCO_3$, $KClO_3$, K_2CrO_4, $Fe(OH)_2$?

2. Write the formulas of a number of other compounds that might be formed from the constituent parts of the above compounds (omitting the atoms within the radicals).

3. Explain the terms: valence, radical, oxidation, reduction.

4. Classify according to the valence of arsenic the following arsenic compounds: $AsCl_3$, As_2O_3, As_2O_5, As_2S_5, $NaAsS_2$ (consider the valence of S to be -2), H_3As, H_3AsO_4, Ag_3As.

5. Complete and balance the following incomplete equations:

$$\begin{aligned}
Fe_2O_3 + C &= CO + \\
Mg(OH)_2 + HCl &= \\
MgO + HNO_3 &= \\
Cr(OH)_3 + H_2SO_4 &= \\
CrCl_3 + KOH &= \\
CrCl_3 + AgNO_3 &= \\
Al + HgCl_2 &= Hg + AlCl_3 \\
NH_4Cl + Ca(OH)_2 &=
\end{aligned}$$

6. In each of the following reactions determine what elements are oxidized and what reduced:

$$\begin{aligned}
2\ HgCl_2 + SnCl_2 &= 2\ HgCl + SnCl_4, \\
2\ AgNO_3 + Zn &= 2\ Ag + Zn(NO_3)_2, \\
Zn + NaOH + H_2O &= NaHZnO_2 + H_2.
\end{aligned}$$

CHAPTER VII

CHEMICAL NOMENCLATURE

The common names of most familiar substances, given before the development of chemistry as a science, usually give no clue to their composition. However, as the number of known substances has increased it has become necessary to use names which are based upon some system. The multiplication of terms such as "oil of vitriol" (which is not an oil), "copperas" (which contains no copper), "Glauber's salt," "cream of tartar," "muriatic acid," etc., would place an almost impossible task upon the memory if it were extended to the hundred thousand or more known substances. To avoid such a situation as is found in mineralogy, where the terms give little clue to the composition of the substance, chemists have evolved a nomenclature which is based upon the elements composing the compound. This nomenclature has the advantage of being almost international, so far as the European languages are concerned.

Names of the Elements. The only generalization possible in the nomenclature of the elements is in regard to the names of the metals. The effort has been to give the Latin neuter suffix, *-um*, to the names of metals, as illustrated by potassium, magnesium, platinum. Where the element was commonly known before the introduction of this systematic nomenclature we may have still surviving the common name without this suffix, as with iron, silver, copper, gold. In

such cases the Latin name, from which the symbol is derived, may, however, often be used to designate compounds. For example, instead of copper sulfate we may say cupric sulfate, from the Latin *cuprum*. The reason for this use of the Latin name will become apparent later.

The group NH_4, which gives compounds analogous to those of the metal potassium, is called ammonium.

The Most Positive Element Named First. It is customary to give the name of the most metallic or positive element first in naming the compound (corresponding to the order used in writing the formula), as is seen in the names of aluminum oxide, sodium chloride, copper sulfide, magnesium sulfate, potassium nitrate, hydrogen fluoride, carbon dioxide, etc.

Binary Compounds Designated by Suffix -ide. When the compound consists of but two elements it is customary to suffix *-ide* to the name of the second or less metallic element in naming the compound. Thus all compounds of oxygen with a single more positive element are called oxides, those of chlorine are called chlorides, those of phosphorus, phosphides, those of carbon, carbides, etc.

In a few cases this suffix is used where the compound contains more than two elements because of the existence of certain groups acting much like a single element. For example, the cyanide group, CN, acts very much like the halogens, hence KCN is called potassium cyanide, by analogy with KCl, potassium chloride.

Designation of Compounds Where the Positive Element May Show Different Valences. As was pointed out in the chapter on valence, there are many elements showing more than one valence in their compounds, so that the simple

naming of the constituents as above leaves an ambiguity as to which of the possible compounds is meant. There are, for example, two chlorides, oxides, etc., of mercury, iron, tin, lead, copper, etc., so that it is not sufficient, in these cases, to speak of mercury chloride, iron chloride, tin oxide, copper sulfide, etc. In most cases the positive elements exhibit but two valences in their compounds, and it is possible to distinguish their two series of compounds by adding the suffixes *-ous* and *-ic* to the name of the positive element, signifying the lower and higher valences respectively. Accordingly, we designate HgCl as mercurous chloride and $HgCl_2$ as mercuric chloride; As_2O_3 as arsenous oxide, and As_2O_5 as arsenic oxide. In many cases the common English name of the element does not lend itself to this usage, as with the elements iron, copper, tin, lead. In such instances the Latin name of the element is used, so that we have $FeCl_2$, ferrous chloride, and $FeCl_3$, ferric chloride, Cu_2O, cuprous oxide, and CuO, cupric oxide, SnS, stannous sulfide, and SnS_2, stannic sulfide.

Another way of distinguishing between different compounds of the same element is by the use of the Latin and Greek numeral prefixes to the names of the elements. These prefixes, up to six, are as follows:

	1	2	3	4	5	6
Latin	Uni-	Bi-	Ter-	Quadri-	Quinque-	Sexa-
Greek	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-

To these we may add the Latin *sesqui-*, meaning one and a half. By the use of these prefixes we can often designate the compound with less ambiguity than by means of the suffixes *-ous* and *-ic*, especially when more than two com-

pounds exist. As examples of the use of these prefixes we may mention CO, carbon monoxide, and CO_2, carbon dioxide, CS_2, called both carbon bisulfide and carbon disulfide, PCl_3, phosphorus trichloride, and PCl_5, phosphorus pentachloride, Cr_2O_3, chromium sesquioxide, and CrO_3, chromium trioxide, Sb_2S_3, (di)antimony trisulfide (antimonous sulfide) and Sb_2S_5, (di)antimony pentasulfide (antimonic sulfide).

The prefix *per-* is used in binary compounds chiefly to denote oxides in which the oxygen is related to the oxygen in hydrogen peroxide, H_2O_2, with an average valence of -1. The most important besides hydrogen peroxide are barium peroxide, BaO_2, and sodium peroxide, Na_2O_2. It is doubtless wise to use the term only with oxides of this type, though this is by no means a uniform practice.

A compound like Fe_3O_4, which is doubtless composed of FeO, ferrous oxide, and Fe_2O_3, ferric oxide, may be designated as ferrous-ferric oxide, though it is usually referred to as " magnetic iron oxide." Similarly, Pb_3O_4 is usually known by its commercial name " red lead."

Binary Acids. Acids consisting of hydrogen and one other element are designated by the prefix *hydro-* and the suffix *-ic*, like HCl, hydrochloric acid; HN_3, hydronitric acid; H_2S, hydrosulfuric acid.

Oxy-acids and Salts. Certain elements capable of assuming more than one valence form two or more acids containing oxygen. In such cases the significance *-ous* and *-ic* in distinguishing higher and lower valence is similar to that used with binary compounds. We have H_2SO_3, sulfurous acid, and H_2SO_4, sulfuric acid; $HCrO_2$, chromous acid, and H_2CrO_4, chromic acid; H_3AsO_3, arsenous acid, and H_3AsO_4, arsenic acid; and HNO_2, nitrous acid, and HNO_3, nitric acid. When

more than two oxygen acids of the same elements exist, the prefixes *hypo-* and *per-* are used, as illustrated in the following table, which shows at the same time the salt designations corresponding to the different types of acid, using the acids of chlorine for illustration:

Acid		Corresponding Salt	
HCl	Hydrochloric	KCl	Potassium chloride
$HClO$	Hypochlorous	$KClO$	Potassium hypochlorite
$HClO_2$	Chlorous	$KClO_2$	Potassium chlorite
$HClO_3$	Chloric	$KClO_3$	Potassium chlorate
$HClO_4$	Perchloric	$KClO_4$	Potassium perchlorate

Sulfo-acids and Salts. There are many cases where sulfur replaces oxygen in salts, though the corresponding acids are not capable of existing free. These are designated in the same way as the oxy-salts, using the prefix *sulf(o)-*, or sometimes *thio-*. We have $KSbO_2$, potassium antimonite, and $KSbS_2$, potassium sulfantimonite, $KSbO_3$, potassium antimonate and $KSbS_3$, potassium sulfantimonate, $KCNO$, potassium cyanate, and $KCNS$, potassium thiocyanate.

In the case of $Na_2S_2O_3$, which seems to be a sulfate with one oxygen atom replaced by a sulfur atom, the name thiosulfate is given.

Complex Halogen Acids and Salts. Similar to the oxy- and sulfo-acids we have others containing the halogens, like H_2PtCl_6, chlor-platinic acid, giving salts called chlor-platinates, H_2SiF_6, fluo-silicic acid (cf. H_2SiO_3, silicic acid), $HAuCl$, chlor-aurous acid and $HAuCl_4$, chlor-auric acid.

Acid and Basic Salts. Many acids have more than one replaceable hydrogen atom in the molecule, and many bases have more than one replaceable hydroxyl group in the

molecule. Sulfuric acid, for example, is called a **dibasic acid** on account of its ability to neutralize two hydroxyl groups. Similarly, H_3PO_4, phosphoric acid, is a tribasic acid. On the other hand, $Mg(OH)_2$, magnesium hydroxide, is a **diacid base** for similar reasons. In such cases it is usually possible to have partial neutralization of either acid or base so as to give either an acid salt or a basic salt. The following equations represent the formation of such salts:

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O,$$
$$KOH + H_3PO_4 = KH_2PO_4 + H_2O,$$
$$2\,KOH + H_3PO_4 = K_2HPO_4 + H_2O,$$
$$Mg(OH)_2 + HCl = Mg(OH)Cl + H_2O.$$

The salts produced in these reactions would be called, respectively, sodium acid (or hydrogen) sulfate, potassium di-hydrogen phosphate, di-potassium hydrogen phosphate and magnesium hydroxy-chloride or basic magnesium chloride.

Sometimes a basic or hydroxy-salt may lose water, becoming an oxy-salt. With bismuth hydroxide, for example, $Bi(OH)_3$, the progressive neutralization with HCl would give first $Bi(OH)_2Cl$, then $Bi(OH)Cl_2$, finally $BiCl_3$. The first of these loses water, becoming BiOCl, a well-known substance called bismuth oxychloride. In naming these two kinds of basic salts chemists are not always careful to distinguish between an oxy-salt and a hydroxy-salt, but there is some justification in this, on account of the uncertainty existing in many cases as to whether the water present in the precipitate is actually combined or not.

Sometimes this oxy-group plays the part of a radical, existing throughout various metathetical reactions. The

radical is then usually designated by the suffix *-yl*, as in BiOCl, bismuthyl chloride, CrO_2Cl, chromyl chloride, UO_2Cl_2, uranyl chloride.

Acid salts may likewise lose water, but the possible types of compounds can best be understood in connection with the various types of partially dehydrated acids.

Partially Dehydrated Acids and Their Salts. If an acid salt like $KHSO_4$, potassium acid sulfate, is heated, it loses water according to the equation,

$$2\,KHSO_4 = H_2O + K_2S_2O_7.$$

The same result is obtained by adding SO_3 to K_2SO_4. With reference to its mode of formation this salt is called potassium pyro-sulfate (from the Greek *pyr*, meaning fire). It may also be called potassium bi-sulfate on account of the extra SO_3 present. This is more evident if the formulas of both the sulfate and the bisulfate are expressed as compounds of acid and basic anhydrides, as was done in Chapter V for many salts, giving $K_2O \cdot SO_3$, and $K_2O \cdot 2\,SO_3$, respectively. There are other examples of this type. When acid is added to a chromate, as K_2CrO_4, instead of getting an acid salt, $KHCrO_4$, there results a bichromate, as represented by the equation,

$$K_2CrO_4 + HCl = (KCl + KHCrO_4) = KCl + \tfrac{1}{2}H_2O + \tfrac{1}{2}K_2Cr_2O_7.$$

There is no great distinction between a bi-salt and an acid salt (in solution it is generally impossible to distinguish them) so that the former name is applied somewhat indiscriminately. Thus $NaHCO_3$, sodium acid carbonate, is often called sodium bicarbonate, though the real bicarbonate, which would be $Na_2C_2O_5$, does not exist. Similarly, $KHSO_4$ may be called

potassium bisulfate. Sometimes it is possible to have still more of the acid anhydride present, as with $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$, called potassium trichromate and tetrachromate, respectively, or in general, polychromate (from the Greek *poly*, meaning many). This again becomes most obvious when the formulas are written in terms of the acid and basic anhydrides, giving $K_2O \cdot 3\,CrO_3$ and $K_2O \cdot 4\,CrO_3$.

With a tribasic acid like phosphoric acid, H_3PO_4, there exist several partial anhydrides, like HPO_3 and $H_4P_2O_7$. The relations between these acids is best brought out by the equations,

$$3\,H_2O + P_2O_5 = 2\,H_3PO_4,$$
$$H_2O + P_2O_5 = 2\,HPO_3 = 2\,H_3PO_4 - 2\,H_2O,$$
$$2\,H_2O + P_2O_5 = H_4P_2O_7 = 2\,H_3PO_4 - H_2O.$$

In the first, H_3PO_4, we have the maximum amount of water, and it is called ortho-phosphoric acid (from the Greek *ortho*, meaning straight, direct). The second, meta-phosphoric acid (from the Greek *meta*, meaning after), may be derived by the simple abstraction of water from the ortho-acid. The third is called pyro-phosphoric acid. The application of these terms to several other acids, as in the following table, will make them clearer:

Acids	Boric	Silicic	Phosphorous	Stannic
Ortho	H_3BO_3	H_4SiO_4	H_3PO_3	H_4SnO_4
Meta	HBO_2	H_2SiO_3	(HPO_2)	H_2SnO_3
Pyro	$H_2B_4O_7$ (also called tetra-)	(Many poly-silicic acids. $H_2O \cdot n SiO_2$)	$H_4P_2O_5$	

It is evident that there is no distinction between a pyro-acid and its salts and a poly-acid, and where there are several

it is not customary to use the prefix pyro- with its ambiguous significance, for although there is but one pyro-phosphoric acid there are a number of poly-silicic acids, which require such distinguishing terms as di-meta-silicic acid for $H_2Si_2O_5$; tri-meta-silicic acid for $H_2Si_2O_7$; di-ortho-silicic acid for $H_4Si_3O_6$, etc. The salts are, of course, designated as for the simpler acids; thus $Na_2H_2P_2O_7$ is di-sodium-di-hydrogen pyro-phosphate, $Na_2B_4O_7$ (borax) is sodium tetra- (or pyro-) borate, K_2SnO_3 is potassium metastannate.

EXERCISES

1. How should each of the following substances be named: CaH_2, H_2S, PbS, $Ni(OH)_2$, $Ni(OH)_3$, Hg_2SO_4, $HgSO_4$, PbO, Pb_3O_4, $CuCO_3$, H_2CO_3, $Hg(NO_3)_2$, $Hg(OH)NO_3$, NH_4Cl, NH_4OH, NH_4HSO_4, $KHNH_4PO_4$, $SbCl_3$, $SbCl_5$, SbOCl, NaCl, NaClO, $AlCl_3$, $Al(OH)_3$, NaH_2AlO_3, $NaAlO_2$, SO_2, H_2SO_3 (cf. H_2SO_4, sulfuric acid), $NaHSO_3$, $Na_2S_2O_5$, SO_3, Sb_2O_3?

2. If H_3AsO_4 is called arsenic acid, what should each of the following be called: $HAsO_3$, H_3AsO_3, $H_4As_2O_7$, $PbHAsO_4$, $KAsS_3$?

3. If K_2MnO_4 is called potassium manganate, what should $KMnO_4$ be called?

4. If H_4SnO_4 is called ortho-stannic acid, what would you call each of the following: H_2SnO_2, $NaHSnO_3$, $NaHSnO_2$, Na_2SnS_3?

5. If KCNO is the only oxygen salt of its type, what should it be called? (CN is the "cyanide" group.) What should each of the following be called: KCNS, HCNO, KCN, HCN?

6. The iron in the salts $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ is bivalent and trivalent, respectively. Which should be called potassium ferro(us) cyanide, and which ferri(c) cyanide?

CHAPTER VIII

QUANTITATIVE RELATIONS INVOLVING SOLUTIONS OF KNOWN CONCENTRATION

In quantitative analysis the most useful reactions are usually those occurring in solution. In such cases the quantities may be determined, not by weighing the pure substance, but by measuring the volume of the solution containing a definite amount of the substance. Thus if a large quantity of a solution of sulfuric acid is made containing, say, 60 g. per liter, the amount of the acid taking part in a certain reaction is very simply found by measuring the volume of this solution required in the reaction. For example, if 25.0 cc. of this solution were used in a certain reaction, then the actual amount of sulfuric acid used would be 0.025 of 60 g., or 1.5 g. Before proceeding on this basis, however, it will be profitable to pause and consider whether the amount of the dissolved substance had better be expressed in grams per liter.

Concentration in Terms of Mols Per Liter. As a type of the reactions in solution used in quantitative analysis, we will consider reactions in which acids and bases neutralize each other. It has been explained already how such equations may easily be written if we are guided by the reaction that is fundamental to all neutralization of acids and bases, *i.e.*, the formation of water from the H of the acid and the

OH of the base. Such equations may then be interpreted in terms either of grams or mols, and correct calculations of weight relations may be made in either terms. It is obvious, however, that simpler numerical relations are obtained using mols rather than grams. In a large number of cases 1 mol of acid will neutralize 1 mol of base; in other cases, like the reaction between NaOH and H_2SO_4, 1 mol of acid neutralizes 2 mols of base. We find it advantageous, therefore, to express concentration in terms of mols per liter, and to indicate this briefly by a suitable prefix to the formula of the substance. Thus 2 M-H_2SO_4 indicates a solution containing 2 mols of sulfuric acid per liter; 0.5 M-H_2SO_4, or $\frac{1}{2}$ M-H_2SO_4 or $M/2$ H_2SO_4 all denote a solution containing 0.5 mol of sulfuric acid per liter. Similar designations are applied to solutions of bases and salts, and even to dissolved substances in general.

Titration. Suppose that it were desired to determine the amount of KOH in a sample of lye solution. We would take a definite amount of the solution, say 4.52 g., and titrate with a suitable acid of known concentration, say 0.5 M-H_2SO_4, measuring, by means of a burette, the volume of acid required to neutralize exactly the lye solution, a suitable indicator being used for this purpose. This process is called **titration.** Suppose that 45.80 cc. of the acid is used; then, since 1 liter of 0.5 M-H_2SO_4 contains 0.5 mol of H_2SO_4, 45.80 cc. will contain 0.0458×0.5 mol, or 0.0229 mol of H_2SO_4. Now we see from the equation,

$$2\ KOH + H_2SO_4 = 2\ H_2O + K_2SO_4,$$

that 1 mol of H_2SO_4 neutralizes 2 mols of KOH, hence, 0.0229 mol of H_2SO_4 will neutralize 0.0458 mol of KOH.

Since 1 mol of KOH is 56.1 g., 0.0458 mol is 0.0458×56.1 g., or 2.57 g. Since, further, 4.52 g. of the solution contain 2.57 g. of KOH, 57.0 per cent of the lye solution is KOH.

Standardizing Solutions. In making solutions of known concentration for titration we must start with some substance that can be weighed, such as benzoic acid, $HC_7H_5O_2$ (only one of the hydrogen atoms has acid properties), or sodium carbonate, Na_2CO_3. If it were desired to make 0.05 M-H_2SO_4, which contains 0.05 mol or 4.9 g. of H_2SO_4 per liter, we would make up a quantity of the solution a little more concentrated than 0.05 M by dissolving about 3 cc. of concentrated acid (density 1.8) in a liter of water. We would next determine accurately the concentration of acid in this solution by titrating a known weight of Na_2CO_3. Suppose that it takes 43.0 cc. of our solution to react with 0.248 g. of Na_2CO_3, according to the equation

$$Na_2CO_3 + H_2SO_4 = H_2O + CO_2 + Na_2SO_4.$$

Since 1 mol of sodium carbonate reacts with 1 mol of the acid, and since 0.248 g. of Na_2CO_3 is 0.00234 mol, the amount of H_2SO_4 is also 0.00234 mol, and as this is dissolved in 43.0 cc. the amount in one liter is $\frac{1000}{43} \times 0.00234$ mol, or 0.0545 mol. This solution may be used in titrations just as it is, or by diluting with the right amount of water the concentration may be adjusted to exactly 0.05 molal. Since 0.05 mol per liter is the same as 0.0545 mol in 1090 cc., if water is added to a liter of the 0.0545 molal solution until the volume becomes 1090 cc., then the concentration of the resulting solution is 0.05 molal, as desired. From this an alkaline solution of desired concentration may then be made up by a similar process.

Chemists are, however, prone to take unnecessary pains to adjust their standard solutions to concentrations expressed by simple numbers. By the aid of a slide rule it is just as easy to calculate the results of titrations where the acid is 0.0545 M as it is when it is exactly 0.05 M.

The Equivalent: Normal Concentration. It is very convenient, in titration, to have various solutions of the same neutralizing power. Although it is true that solutions of such acids as HCl and HNO_3 of the same molal concentration may be used interchangeably in titrating bases, solutions of molal HCl and molal H_2SO_4, for example, could not be used indiscriminately, since 1 mol of H_2SO_4 has twice the power that 1 mol of HCl has to neutralize alkali. Similarly, while 10 cc. of 0.1 M-HCl would neutralize 10 cc. of 0.1 M-NaOH, it would neutralize only 5 cc. of 0.1 M-$Ba(OH)_2$. Since, in titrating acids and bases, we are interested in the hydrogen of the acid and the hydroxyl of the base, the simplest basis for making and using such solutions is the amount of acid hydrogen and basic hydroxyl in a liter of the solution. Solutions of NaOH and $Ba(OH)_2$ would have the same neutralizing power if equal volumes contained, not 1 mol of each, but 1 mol and $\frac{1}{2}$ mol, respectively. The amounts of acids and bases to be dissolved in equal volumes of solution are the amounts which, in the particular reactions involved, will yield 1 g. of acid hydrogen and 17 g. of basic hydroxyl, respectively. This amount is called an **equivalent**, and concentration expressed in equivalents is called **normal concentration**, and denoted by the letter N, in the same way that molal concentration is indicated by M. Thus 2 N-H_2SO_4 denotes 2 equivalents of this acid per liter; 0.5 N-KOH denotes 0.5 equivalent of KOH

per liter. Obviously, whenever the acid and base contain one acid hydrogen atom and one hydroxyl group in the molecule, the mol and equivalent are the same, and so molal and normal concentrations of such acids and bases are the same.

Summary. By way of summary it may be stated that any kind of problem involved in titrating acids and bases may be solved by understanding the three following factors, utilizing them in the connection demanded by the problem:

First, the number of equivalents and the number of grams per mol of substance, as indicated by the formula; *e.g.*, $Ca(OH)_2$ denotes 1 mol, 2 equivalents, 74 g.

Second, the meaning of the symbols expressing concentration; *e.g.*, 0.01 *M*-$Ca(OH)_2$ denotes a solution of 0.01 mol (hence, by the first step, 0.02 equivalent or 0.74 g.) of $Ca(OH)_2$ per liter.

Third, the relation between the amount of acid and base used, which is given by the equation, if amounts are expressed in mols or grams, or without the necessity of considering the equation if equivalents are used, since 1 equivalent of any acid neutralizes 1 equivalent of any base, by the definition of the term equivalent.

Examples. What is (1) the molal concentration and (2) the normal concentration when 7.4 g. of $Ca(OH)_2$ is in 2 liters of solution? 1 mol of $Ca(OH)_2$ is 2 equivalents, and weighs 74 g., hence 7.4 g. is 0.1 mol and 0.2 equivalent. Since this is dissolved in 2 liters, 1 liter would contain 0.05 mol or 0.1 equivalent, so that the solution would be 0.05 molal or 0.1 normal, expressed briefly as 0.05 *M*-$Ca(OH)_2$ and 0.1 *N*-$Ca(OH)_2$, respectively.

How many cc. of 0.2 *N*-HCl will be required to neutralize 40.0 cc. of 0.5 *N*-NaOH? By 0.5 *N*-NaOH we mean 0.5

equivalent of NaOH in 1 liter of solution, hence 40.0 cc. of it, which is 0.040 liter, will contain 0.040×0.5 equivalent, or 0.02 equivalent of NaOH. Since 1 equivalent of any acid neutralizes 1 equivalent of any base, the amount of acid neutralized by 0.02 equivalent of NaOH is 0.02 equivalent. Since 0.2 *N*-HCl means 0.2 equivalent of it per liter of solution, to get 0.02 equivalent we would have to take 0.1 liter, or 100 cc.

It was found that the acetic acid in 10 cc. of vinegar was neutralized by 14.0 cc. of 0.5 *M*-KOH solution. How many grams of acetic acid were in 100 cc. of the vinegar? The formula of acetic acid is $HC_2H_3O_2$, and only one of the hydrogen atoms in the molecule has acid properties. By 0.5 *M*-KOH we mean a solution containing 0.5 mol of KOH per liter. Since 14 cc. is 0.014 liter, this volume of solution will contain 0.014 of 0.5 mol, or 0.007 mol of KOH. By writing the equation,

$$KOH + HC_2H_3O_2 = H_2O + KC_2H_3O_2,$$

we see that 1 mol of the acid neutralizes 1 mol of the base, so that 0.007 mol of the base will be neutralized by 0.007 mol of the acid, which is the amount present in 10 cc. of vinegar. Since 1 mol of acetic acid weighs 60 g., 0.007 mol weighs 0.42 g. Since this amount is contained in 10 cc. of vinegar, 100 cc. would contain 4.2 g.

If 0.654 g. of zinc is completely dissolved in 100 cc. of 0.5 *M*-H_2SO_4, what will be the concentration of the acid after the reaction, in terms of: (1) mols per liter, (2) equivalents per liter? The atomic weight of zinc is 65.4, so that 0.654 g. is 0.01 gram-atom of zinc. From the equation for the reaction,

$$Zn + H_2SO_4 = ZnSO_4 + H_2,$$

we see that 1 gram-atom of zinc will use up 1 mol of acid, hence, 0.01 gram-atom of zinc would use up 0.01 mol of the acid. Now 1 liter of 0.5 M-H_2SO_4 contains 0.5 mol, and 100 cc. would contain 0.05 mol. The zinc used up 0.01 mol of this, leaving 0.04 mol of H_2SO_4 in 100 cc., which corresponds to 0.4 mol per liter. Since 1 mol of H_2SO_4 = 2 equivalents, 0.4 mol = 0.8 equivalent and the solution may be called 0.8 normal.

Titration Involving Other Types of Reaction. It will be seen from the last example above that solutions of known concentration may be used to measure amounts of material in other reactions besides those where acids and bases neutralize each other. The speed with which volumes of solutions can be measured in titrations, the process called **volumetric analysis**, compared with that required for getting the products of reactions into weighable form, **gravimetric analysis**, makes the former desirable wherever speed is desired. When neutralization of acids and bases does not take place, some other means of indicating the " end-point " of the reaction is necessary. Where a highly colored substance disappears in the reaction, this may be used to indicate when the exact amount required has been added. Any excess makes itself evident by reason of the color. One such substance frequently used is potassium permanganate, $KMnO_4$, a substance with a deep purplish red color, which is a very strong oxidizing agent. As an example of the type of reaction now being considered, let us determine how much iron is in an ore, 1.016 g. of which, when dissolved in acid so as to give a solution containing $FeSO_4$, required 45.0 cc. of 0.5 M-$KMnO_4$ to change the $FeSO_4$ to $Fe_2(SO_4)_3$, according to the equation,

$$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O.$$

The actual amount of $KMnO_4$ used is evidently 0.045 of 0.5 mol, or 0.0225 mol. According to the equation 2 mols of $KMnO_4$ react with 10 mols of $FeSO_4$, so that 0.0225 mol of $KMnO_4$ would react with 5×0.0225 mol, or 0.1125 mol of $FeSO_4$. Now 0.1125 mol of $FeSO_4$ contains 0.1125 gram-atom of iron, and since 1 gram-atom of iron is 55.8 g., 0.1125 gram-atom would weigh 0.1125×55.8 g., or 0.626 g. Since, finally, this amount of iron was found from 1.016 g. of the ore, the iron is 61.7 per cent of the ore.

EXERCISES

1. Write equations expressing the neutralization of sodium hydroxide with hydrochloric acid; sodium hydroxide with sulfuric acid; calcium hydroxide with nitric acid; barium hydroxide with sulfuric acid.

2. Write under each substance involved in the above equation the number of mols, grams and equivalents represented.

3. How many grams are there in 1 equivalent of each of the following substances: KOH, H_2SO_4, H_2S, $Al(OH)_3$? From your answers state how many grams of aluminum hydroxide and sulfuric acid would combine to form aluminum sulfate.

4. How many mols of sulfuric acid will be neutralized by 4 equivalents of sodium hydroxide? *Ans.* 2 mols.

5. If 0.98 g. of sulfuric acid is in 1 liter of solution, what is (*a*) the molal concentration? (*b*) the normal concentration? *Ans.* (*a*) 0.01 *M*; (*b*) 0.02 *N*.

6. When 3.7 g. of calcium hydroxide are in 5 liters of solution, what is (*a*) the molal concentration? (*b*) the normal concentration? *Ans.* (*a*) 0.01 *M*; (*b*) 0.02 *N*.

7. (*a*) How many equivalents of barium hydroxide are in 200 cc. of 0.1 normal solution? (*b*) How many mols? (*c*) How many equivalents of hydrochloric acid could this solution neutralize? (*d*) How many grams?

8. If 10 cc. of a certain solution of sulfuric acid neutralized 20 cc. of a normal solution of potassium hydroxide, what was the concentration of the former in (*a*) equivalents per liter: (*b*) mols per liter; (*c*) grams per liter? *Ans.* (*a*) 2 *N*; (*b*) 1 *M*; (*c*) 98 g. per liter.

9. If 25 cc. of 0.2 normal acid neutralized some base, how many equivalents of base were there? How many grams of base were there if the base was (*a*) sodium hydroxide; (*b*) calcium hydroxide?
Ans. 0.005; (*a*) 0.2 g.; (*b*) 0.185 g.

10. If 10 cc. of *N* /5 ammonium hydroxide neutralizes 20 cc. of sulfuric acid, what was the concentration of the latter?
Ans. 0.1 *N*.

11. How many cc. of 0.2 normal acid are necessary to neutralize 25 cc. of 0.5 normal alkali? *Ans.* 62.5 cc.

12. How many grams of hydrogen peroxide, H_2O_2, were present in a solution which required 40.0 cc. of 0.05 *M*-$KMnO_4$ to react according to the following equation:

$$5\ H_2O_2 + 2\ KMnO_4 + 3\ H_2SO_4 = 5\ O_2 + 8\ H_2O + K_2SO_4 + 2\ MnSO_4?$$

Ans. 0.17 g.

CHAPTER IX

THERMOCHEMISTRY

THERE are many chemical reactions in which our interest lies ordinarily not in the substances produced but in the heat evolved or absorbed. The burning of fuels is a chemical reaction, but our purpose in burning them is not to produce the carbon dioxide and water that usually result. These substances we take pains to dispose of by means of chimneys and ventilation. Our purpose is rather to obtain the heat or light that accompanies the reaction. In buying fuels, therefore, the important consideration is not the relative cost of the various available fuels but the relative cost of the heat as obtained from each. The chemist should therefore know how the heat of such a reaction may be measured and expressed.

Again, in many reactions of importance, a knowledge of whether heat is absorbed or evolved helps to determine the most desirable conditions for carrying it out, as will be explained in Chapter XIV. Also in technical processes, if heat is absorbed during a reaction, this may have to be considered in estimating the cost, since the heat thus absorbed may have to be supplied by means of fuel or electrical energy.

The Calorie. The unit in which heat is most conveniently measured is the calorie (abbreviated cal.). This is the amount of heat required to raise the temperature of 1 g.

of water 1° C.* Since many heats of reaction involve many thousand calories it is also customary to use a larger unit, the kilogram calorie (abbreviated Kal.). This is the heat required to raise the temperature of 1 kilogram of water 1° C. Obviously, 1 Kal. = 1000 cal.

Experimental Determination of Heats of Reaction. The amount of heat involved in a chemical reaction is determined in an apparatus known as a calorimeter. It consists of a vessel holding perhaps a liter of water, provided with a stirrer and a more or less delicate thermometer. This vessel must be well surrounded by some effective heat insulator, so that the temperature of the water within shall be affected only to the least possible extent by the room temperature. This insulation may be furnished by felt, a water jacket, or, often best of all, by a vacuum jacket, as in a Dewar flask. (This is the vessel that has been adapted to household and picnic use and sold under such names as "Thermos," "Caloris," etc.) The reacting substances may be introduced into the calorimeter in various ways. When the heat of solution of a solid is to be measured the substance may be sealed in a thin glass bulb immersed in water in the calorimeter. After uniform temperature has been reached the bulb is broken and the solid allowed to dissolve. If the reaction is one like the precipitation of

* In very accurate work it is necessary to specify the temperature of the water, for the amount of heat required to produce the same elevation in temperature is not the same at all temperatures. We thus have the "zero calorie," the "15° calorie" and the "mean calorie," which is the average value between 0° and 100° C.

It is possible also to express the quantity of heat in terms of other energy units, since the relation between these different kinds of energy is known. A unit frequently used is the joule, which is 10^7 ergs, or 1 volt-coulomb, or $\frac{1}{4.18}$ cal.

an insoluble substance from dilute solutions, or the neutralization of an acid by a base, one liquid may be inclosed in a thin glass vessel, or in one with a valve, and immersed in the other liquid. The liquids may then be mixed at the proper time. If the reaction is one taking place at a high temperature, it may be carried on within a " bomb " immersed in the water of the calorimeter. A small weighed portion of the material under investigation is placed within this bomb, which is then closed and filled through a tube in the top with oxygen under high pressure. It is then placed in the calorimeter and when uniform temperature is attained the combustion is brought about by means of an electrical connection through the lid of the bomb.

The amount of heat liberated by the reaction is measured by the rise in temperature of the calorimeter contents and the heat capacity of the latter. If water alone were involved, the number of calories liberated would be found simply by multiplying the rise in temperature by the weight of the water. Various other substances are present, however, such as the stirrer, the containing vessel, the thermometer, etc., so that their power of absorbing heat compared with that of water must be measured or calculated and added to the weight of the water as the " water equivalent " of the calorimeter. This may be measured by allowing a reaction evolving a known amount of heat to take place in the calorimeter, or else calculated, by knowing the heat capacities or specific heats, together with the weights of the various substances in the calorimeter.

The Numerical Representation of Heats of Reaction. In expressing the results of thermochemical measurements it is usual to include in the equation the number of calories

evolved or absorbed. The amounts of substances represented by the equation are understood to be expressed in mols. Thus the equation,

$$C + O_2 = CO_2 + 96{,}500 \text{ cal.},$$

indicates that when 1 mol (12 g.) of carbon burns with 1 mol of oxygen to form 1 mol (44 g.) of carbon dioxide, 96,500 cal. of heat are evolved. This amount of heat is also called the " heat of formation " of carbon dioxide from its elements.

Similarly, the equation,

$$N_2 + O_2 = 2\,NO - 43{,}200 \text{ cal.},$$

means that when 1 mol (28 g.) of nitrogen reacts with 1 mol (16 g.) of oxygen to form 2 mols (30 g.) of nitric oxide, 43,200 cal. of heat are *absorbed*. This reaction might equally well be written

$$N_2 + O_2 + 43{,}200 \text{ cal.} = 2\,NO.$$

The ordinary rules of algebra apply to the sign of the heat if the number is thus transposed. Either way of writing the equation signifies that nitrogen, oxygen and heat are all used up in the formation of nitric oxide.

The term **exothermic** is often applied to reactions which evolve heat and **endothermic** to those which absorb heat. It may be mentioned that the former predominate in reactions occurring at ordinary temperatures and the latter in those occurring at very high temperatures, in the electric furnace.

Effect of the State of the Reacting Substances. The heat of a reaction depends upon the temperature at which it is carried out and upon the state of the substances involved. For example, in the union of hydrogen and oxygen

to form water, it makes a difference whether the water produced is at a temperature at which it is liquid or vapor. Since the condensation of steam to liquid takes place with the evolution of heat, it is evident that where the final product is liquid the heat of formation will be greater than when it is a gas. To make this clear we will need to specify in the equation the state of the substance, which we would do in this case as follows:

$$2\,H_2 + O_2 = 2\,H_2O\ (\text{gas}) + 67{,}800\ \text{cal., or}$$
$$= 2\,H_2O\ (\text{liq.}) + 68{,}400\ \text{cal.}$$

Or, again, we might find it desirable to express the states of all substances in the equation where ambiguity might otherwise arise, as in the equation,

$$Hg\ (\text{liq.}) + Cl_2\ (\text{gas}) = HgCl_2\ (\text{solid}) + 53{,}300\ \text{cal.}$$

It makes a difference also whether or not a substance is in solution, and what its concentration in the solution is. We might, therefore, have an equation like the following:

$$NaOH\ (0.1\ \text{molal}) + HCl\ (0.1\ \text{molal}) =$$
$$H_2O + NaCl\ (0.05\ \text{molal}) + 13{,}700\ \text{cal.}$$

Where the concentration is small and does not need to be specified exactly, it may suffice to use the abbreviation aq. after the formula of the dissolved substance, which signifies the presence of a large amount of water. (From the Latin *aqua*, water.)

In a gaseous reaction, in which the number of molecules of gaseous substances changes, the heat will be somewhat different if the reaction is carried out in a closed vessel, so that the volume remains constant, from what it will be if the

reaction is carried out so as to keep the pressure constant. Since a gas does work in expanding against an external pressure, heat must be absorbed during the expansion in order to maintain the original molecular velocity and hence the original pressure. This behavior finds illustration in the fact that a ball thrown against a yielding surface rebounds with less speed than when thrown against a rigid surface. The heat of a chemical reaction at constant pressure will therefore be greater or less than that of the same reaction at constant volume according as the number of gaseous molecules decreases or increases during the reaction.

Indirect Determination of Heats of Reaction. In many cases the heat of a reaction cannot be determined directly on account of the difficulty of carrying out the reaction in a calorimeter. In such cases it is usually possible to determine it indirectly. Moreover, even though the reactions may be easily carried out in the calorimeter it is unnecessary to measure the heats of all, since some may be calculated from others. To do this we use a well-founded law stating that all heats of reaction depend only on the state of the initial or final substances and not upon the steps into which the reaction may be divided. This law is a consequence of the more fundamental law of the conservation of energy, which states that though energy be transformed from one form to another, none of it is ever lost. The different forms of energy include heat, potential energy, or energy of position, kinetic energy, or energy of motion, electrical energy, chemical energy, etc. As an example, $ZnSO_4$ might be formed from its elements in either of the following ways:

First Way

$$Zn + \tfrac{1}{2} O_2 = ZnO + 85 \text{ Kal.}$$
$$S + O_2 = SO_2 + 70 \text{ Kal.}$$
$$SO_2 + \tfrac{1}{2} O_2 = SO_3 + 22 \text{ Kal.}$$
$$ZnO + SO_3 = ZnSO_4 + 53 \text{ Kal.}$$
$$\text{Total: } Zn + S + 2\,O_2 = ZnSO_4 + 230 \text{ Kal.}$$

Second Way

$$Zn + S = ZnS + 40 \text{ Kal.}$$
$$ZnS + 2\,O_2 = ZnSO_4 + 190 \text{ Kal.}$$
$$\text{Total: } Zn + S + 2\,O_2 = ZnSO_4 + 230 \text{ Kal.}$$

The total result in either case is the formation of $ZnSO_4$ from Zn, S and $2\,O_2$ with the evolution of heat. Our law tells us that the total heat liberated is the same in either case, as shown by the above figures.

As a consequence of this, thermochemical equations may be added or subtracted like any algebraic equations. Suppose that the following heats of reaction have been measured:

$$C + O_2 = CO_2 + 96.5 \text{ Kal.}, \quad (1)$$
$$\text{and } 2\,CO + O_2 = 2\,CO_2 + 135.0 \text{ Kal.}, \quad (2)$$

and we wish to learn the heat of the reaction

$$2\,C + O_2 = 2\,CO.$$

All that is necessary is to eliminate CO_2 from equations (1) and (2) by multiplying (1) by 2 and subtracting (2) from it, obtaining

$$2\,C - 2\,CO + O_2 = 58 \text{ Kal.},$$

or, transposing,

$$2\,C + O_2 = 2\,CO + 58 \text{ Kal.}$$

If, on the other hand, we eliminate O_2 by subtracting (1) from (2), we obtain the equation for a different reaction,

$$2\,CO = C + CO_2 + 38.5\ \text{Kal.},$$

which, since it usually reacts in the reverse direction, we may prefer to write

$$C + CO_2 = 2\,CO - 38.5\ \text{Kal.}$$

Again, it is not possible to synthesize H_2O_2 aq. from its elements in the calorimeter, but the heat that would be evolved if the reaction were possible may be calculated from the following:

$$H_2O_2\ \text{aq.} = H_2O + \tfrac{1}{2}\,O_2 + \text{aq.} + 23.0\ \text{Kal.},$$
$$H_2 + \tfrac{1}{2}\,O_2 = H_2O + 68.4\ \text{Kal.}$$

Subtracting the first from the second to eliminate H_2O we obtain

$$H_2 + \tfrac{1}{2}\,O_2 - H_2O_2\ \text{aq.} = -\tfrac{1}{2}\,O_2 - \text{aq.} + 45.4\ \text{Kal.},$$

or, transposing to make the signs positive,

$$H_2 + O_2 + \text{aq.} = H_2O_2\ \text{aq.} + 45.4\ \text{Kal.}$$

From this we learn that H_2O_2 is an exothermic compound, formed *from its elements* with the evolution of heat.

Fuel Value of Foods. The heat evolved by the combustion of dry food materials in a calorimeter bomb serves for an approximate valuation of their ability to furnish the heat and muscular energy needed by the body. Accordingly, the amount of food materials needed per day can be estimated roughly by the aid of a knowledge of the fuel values of the foods. An adult needs from 2000 to 3500 Kal. per day, according to his weight and to the amount of his muscular activity. This makes it possible, for example, to cal-

culate roughly the quantity of food needed, and the relative costs of different foods, which aids in reducing costs of food in the home and in institutions, and furnishes a valuable means of determining the least weight of food necessary for a camping or exploring expedition. It may be of interest to have the few figures given in the following table:

Foods	Approximate Number Kal. per Pound
Starchy foods, cereals, flour, rice, beans, etc.	1650
Sugar	1860
Fats and oils	3650
Cheese	2000
Chocolate	2850
Milk, evaporated, unsweetened	800
Milk, condensed, sweetened	1500
Dried fruit	1300
Fish	1000
Meat	1600

Of course, other considerations must also enter to secure a wholesome well-balanced diet, but these cannot be discussed here.

EXERCISES

1. What is the distinction between heat and temperature?

2. Calculate the heat of the reaction

$$CaO + CO_2 = CaCO_3$$

from the following:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O + 30.5 \text{ Kal.},$$
$$CaO + H_2O = Ca(OH)_2 + 11.5 \text{ Kal.}$$

Ans. 42.0 Kal.

3. Calculate the heat of the reaction

$$Zn + Cl_2 + \text{aq.} = ZnCl_2\,\text{aq.}$$

from the following determinations:

$$Zn + 2\,HCl\,\text{aq.} = ZnCl_2\,\text{aq.} + H_2 + 36 \text{ Kal.},$$
$$H_2 + Cl_2 = 2\,HCl\,(\text{gas}) + 44 \text{ Kal.},$$
$$HCl\,(\text{gas}) + \text{aq.} = HCl\,\text{aq.} + 17 \text{ Kal.}$$

4. (*a*) Calculate the heat of the reaction

$$N_2 + 3\ H_2 = 2\ NH_3$$

from the following:

$$4\ NH_3 + 3\ O_2 = 2\ N_2 + 6\ H_2O\ (\text{liq.}) + 364\ \text{Kal.},$$
$$H_2 + \tfrac{1}{2}\ O_2 = H_2O\ (\text{liq.}) + 68.4\ \text{Kal.}$$

Ans. 23.2 Kal.

(*b*) The above figures are for constant pressure; would the heat of formation of NH_3 be greater or less at constant volume?

5. Given that $C + O_2 = CO_2 + 96.5$ Kal., and that anthracite coal, considered as 95 per cent carbon, costs \$10 per ton (= 1000 kg.), determine the cost of 1000 Kal. from the burning of this coal.

Ans. 0.13 cent

6. Considering "water gas" to consist of CO and H_2 only as indicated by the equation of its formation,

$$C + H_2O = CO + H_2,$$

and given the heats of combustion of CO and H_2, *i.e.*,

$$CO + \tfrac{1}{2}\ O_2 = CO_2 + 68.0\ \text{Kal.},$$
$$H_2 + \tfrac{1}{2}\ O_2 = H_2O + 68.5\ \text{Kal.},$$

calculate the cost of 1000 Kal. from this gas if it costs 90 cents per 1000 cu. ft. (= 28,300 liters) when measured at 20° C. and 1 atm. pressure. *Ans.* 1.12 cents.

7. If kerosene were pure $C_{10}H_{22}$, whose heat of combustion is 1626 Kal., and costs 15 cents per gallon (3.781 liters) and has a density of 0.79 g. per cc., calculate the cost of 1000 Kal. obtained by burning kerosene. *Ans.* 0.44 cent.

8. From the table on page 122 make out a "grub-list" for two men on a ten-day walking tour, endeavoring to get the minimum weight consistent with variety and palatability.

CHAPTER X

BEHAVIOR OF SUBSTANCES DISSOLVED IN WATER. IONIC THEORY

Such a large proportion of the reactions with which we concern ourselves take place in water solution that the behavior of substances dissolved in water is a subject of great importance. We will consider a number of the properties and reactions of substances in aqueous solution, and see what conclusions may be drawn as to the nature of these solutions.

Abnormally Great Lowering of the Freezing Point. It has been pointed out in Chapter III that the molecular weight of substances may be determined by two essentially different methods. One depends upon the property of a mol of any substance in the gaseous form to occupy 22.4 liters at 0° C. and 1 atmosphere. The other depends upon the ability of 1 mol of any substance, when dissolved in a given amount of a certain solvent, to exert the same effect upon the escaping tendency of the solvent, as measured by the freezing point, boiling point or vapor pressure. For example, we may define a mol, experimentally, as the number of grams of substance which, in the vapor state at 0° C. and 1 atmosphere, will occupy 22.4 liters, or else as the number of grams which, dissolved in 1000 g. of water, will lower the freezing point of the water 1.86°. If we determine the effect of various substances on the freezing point of water, we find that a large number of substances show concordant be-

havior. Other substances, including acids, bases and salts, show an abnormally great lowering of the freezing point. This is illustrated in the following table:

Substance	Freezing Points of 0.1 Molal Solution
Sugar	−0.188°
Glycerine	−0.186
Alcohol	−0.184
NaCl	−0.348
HCl	−0.356
KNO_3	−0.330
$BaCl_2$	−0.478
Na_2SO_4	−0.459

It will be seen that the first three substances in the table behave as would be expected, but that the others give an abnormally great lowering of the freezing point. There are two ways of accounting for this abnormality. Either the law of the uniform molal lowering does not hold universally, or else acids, bases and salts dissociate into two or more independent parts when dissolved in water. If this law still holds, then 1 mol of NaCl, HCl or KNO_3, when dissolved in a large quantity of water, seems to yield nearly 2 mols of dissolved substances, whereas 1 mol of $BaCl_2$, or of Na_2SO_4, seems to yield nearly 3 mols of dissolved substances.

Now we have, with some substances, examples of an abnormally great molal volume when in the vapor state. When 1 mol of NH_4Cl is vaporized at 1 atmosphere and 350° C., instead of occupying a volume $\frac{6}{2}\frac{2}{7}\frac{3}{3} \times 22.4$ liters, or 51.2 liters, it occupies twice that volume. In this case it is possible to show that the vapor contains HCl and NH_3, uncombined, so that dissociation of the ammonium

chloride molecule into two other molecules has actually taken place. Before abandoning, therefore, the similar conclusion in connection with the effect of dissolved substances on the freezing point of the solvent, let us see whether there are any other phenomena which indicate that acids, bases and salts are dissociated into simpler parts when dissolved in water.

If such dissociation occurs, what can be the nature of these resultant mols? Does a solution of NaCl contain sodium and chlorine? The properties of elementary sodium and chlorine are evidently not those of a solution of sodium chloride, sodium being a metal that reacts violently with water, and chlorine being a very corrosive poisonous substance, whose aqueous solution has a greenish color. When the dissociation theory was first advanced, some chemists made such objections with much effect. However, let us consider some other properties of these solutions, to see if we can deduce a more plausible idea of the nature of the products of the dissociation indicated by freezing point lowering.

Independent Migration of Ions in Electrolysis. It has been found that all dissolved substances that give the abnormal effect on the freezing point of water also give solutions which conduct the electric current, depositing materials at the electrodes, or else dissolving the electrodes. Because of this behavior they are called **electrolytes**. Those conducting very well, the strong acids and alkalis, and most salts, are called **strong electrolytes**. The only satisfactory way to account for this conducting power is to assume that the solution contains charged substances which travel towards the positive and negative poles respectively; and that on

their arrival at the electrodes their charges are neutralized, so that uncharged substances are there deposited. It is indeed possible to detect this migration experimentally. If, for example, we have a **U**-tube containing, say, dilute

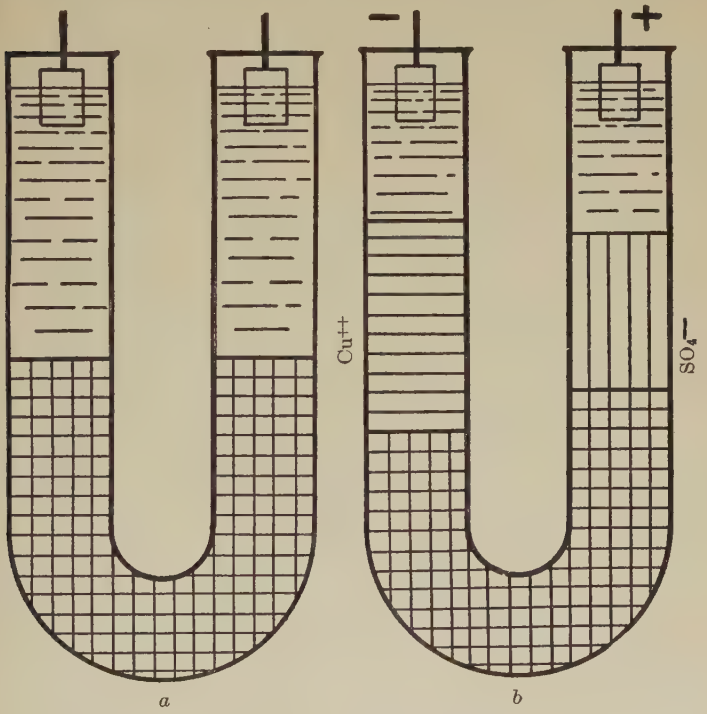


Fig. 10. — Migration of Ions in Electrolysis.

copper sulfate in the bottom, with dilute potassium nitrate carefully superimposed, as shown in Fig. 10, *a*, and allow an electric current to pass through the solution for a time, we will find that the blue color characteristic of copper salts

travels towards the negative pole, while the sulfate radical travels towards the positive pole, as might be shown by testing layers of solution with a solution of barium chloride. The state of affairs after the passage of current is depicted in the figure at *b*. Whenever electrolysis takes place it is possible to show such independent migration of the two parts of the salt, acid or base by appropriate experiments similar to the above.

The Dissolved Ions Carry Definite Electric Charges. The salt, acid or base is thus found to consist of two parts, one of which travels to the negative pole, or **cathode**, the other to the positive pole, or **anode**. On account of their migration these parts are called **ions**, from the Greek word *io*, meaning to go. The ion which travels toward the cathode is called the cation, the one traveling towards the anode, the anion. On account of this migration in electrolysis we are led to conclude that the products of dissociation are charged electrically, the cation being positive and the anion negative. The difficulty of imagining such substances in solution as sodium and chlorine is overcome by this discovery of positively charged sodium, called sodium ion, a totally different substance, and negatively charged chloride ion, a substance quite different from free chlorine. The ions must not be confused, therefore, with the uncharged metals or non-metals, or radicals, which are quite different substances, as seen by their fundamentally different properties. Thus copper ion, a greenish-blue substance existing only in solution, giving precipitates with dilute sodium hydroxide or carbonate, etc., is as different from copper, a reddish, rather heavy metal, as both are from the third substance, copper bromide, a brown salt.

We can prove further that copper ion and copper differ by a positive charge, by actually changing one into the other by adding or removing the charge. If the blue solution of a copper salt is electrolyzed, copper deposits on the cathode, where the positive charge on the copper ion is neutralized. Again, if copper is made the anode or positive pole, in a solution of a salt such as sodium chloride or sulfate, the positive charge sent to the anode changes the copper to copper ion which goes into solution, giving it a blue color.

The amount of the charge on the various ions is not always the same, but a simple and important relationship exists between the charge and the amount of substance. To deposit 1 gram-atom of any univalent substance, like hydrogen, sodium, silver, chlorine, etc., requires 96,540 coulombs of electricity.* The importance of this quantity is therefore very great, and it is called a **faraday** of electricity, in honor of the English physical chemist, Michael Faraday, who discovered the above law. For example, since 108 g. of silver equal a gram-atom, to deposit 1 g. would require $\frac{1}{108}$ of 96,540 coulombs, and to deposit 5 g. would require $\frac{5}{108}$ of 96,540 coulombs, or 4470 coulombs. If this were done by a current of 2 amperes (2 coulombs per second), the time required would be 2235 seconds, or 37 minutes, 35 seconds. However, to deposit 63.6 g. of copper, from ordinary copper salts, 64.5 g. of zinc, etc., requires twice as much electricity, or 2 faradays. Similarly, certain other ions require 3 faradays per gram-ion. We will therefore indi-

* A coulomb is the amount of electricity carried by a current of 1 ampere in 1 second; *e.g.*, 10 amperes flowing for 1 minute would amount to 600 coulombs, and if 1000 coulombs are delivered in 50 seconds, the current strength is 20 amperes.

cate in the formula of the ion the amount of electricity carried by it, and designate the foregoing ions by the following formulas: H^+, Cl^-, Ag^+, Cu^{++}, Zn^{++}, where the number of charges written indicates the number of faradays of electricity per gram-atom, and the sign indicates whether the charge is positive or negative. Since we start with an uncharged salt, the total charges on the ions produced when it dissolves in water must add up to zero. The following equations are given by way of illustration:

$$CuSO_4 = Cu^{++} + SO_4^{--},$$
$$HCl = H^+ + Cl^-,$$
$$KCl = K^+ + Cl^-.$$
$$KOH = K^+ + OH^-,$$
$$K_2SO_4 = 2\,K^+ + SO_4^{--},$$
$$Cu(NO_3)_2 = Cu^{++} + 2\,NO_3^-.$$

In general the metal constituent of a salt or base, and the hydrogen of acids, yield the cations, or positive ions, while the remaining portion of the compound, the hydroxyl (OH) of bases, or the " acid radical " of acids and salts, yield the anions, or negative ions. The signs of the electric charges correspond to and justify the differentiation into positive and negative constituents made in Chapter VI in assigning algebraic signs to valences. The valence must be identical both as to magnitude and sign with the charge on the ion. Hydrogen in practically all of its compounds has a valence of + 1, and when these compounds dissociate on dissolving in water they yield hydrogen ion with one positive charge, H^+. Chlorine in the metallic chlorides has a valence of − 1, both from the point of view of its relation to hydrochloric acid, HCl, and also from the formula of chloride ion, Cl^-.

In $AlCl_3$ aluminum is considered trivalent, either from the fact that it has replaced 3 hydrogen atoms, or from the formula of the ion, Al^{+++}, which results on dissolving the chloride in water.

The formulas of the two ions formed from any electrolyte on dissociation and the formula of the undissociated substance are connected so that any two of them will serve to predict the third. Thus, knowing the formula of sulfuric acid, H_2SO_4, and that of hydrogen ion, H^+, we can determine the formula of the sulfate ion by writing the equation for the dissociation, remembering that the total amount of positive and negative electricity in the solution must be the same, since the pure substances which form the ions on dissolving are uncharged. Taking away two positive hydrogen ions from H_2SO_4 would leave therefore SO_4^{--}.

Knowing, now, the formula of sulfate ion, and given that of another sulfate, like ferric sulfate, $Fe_2(SO_4)_3$, we get

$$Fe_2(SO_4)_3 = 2\,Fe^{+++} + 3\,SO_4^{--}.$$

Again, if we know the following ionic formulas, K^+, Ca^{++}, Fe^{+++}, SO_4^{--}, PO_4^{---}, by remembering that the solid compounds formed from them would be uncharged, we can write the formulas of the compounds of these ions, *i.e.*, K_2SO_4, K_3PO_4, $CaSO_4$, $Ca_3(PO_4)_2$, $Fe_2(SO_4)_3$ and $FePO_4$.

The Atom of Electricity. We see that the amount of electricity combined with any gram-atom in an ion is always some simple multiple of the faraday. Furthermore, we have different ions of the same element, in some cases, in which the number of faradays per gram-atom in one is a simple multiple of what is in the other. This is exemplified by

Fe^{++} and Fe^{+++}, Hg^{+} and Hg^{++}, Sn^{++} and Sn^{++++}, Cu^{+} and Cu^{++}. The two ions of each metal are radically different substances. We thus have a law corresponding to the law of simple multiple proportions by weight, as explained in Chapter III, and just as that law led logically to the atomic theory, so the similar law of simple multiple proportions of electricity per gram-atom of substance leads logically to an atomic theory for electricity, a theory which has been abundantly confirmed by independent evidence.

We may thus regard the number of plus or minus signs written in the formulas of ions as indicating the number of atoms of electricity, positive or negative, in a single ion. However, there seems to be but one kind of electricity, negative electricity, involved in these changes; a positive electric charge on an atom is therefore the result of the removal of negative electricity. At present it seems that we must regard an ion like chloride ion as a compound of a chlorine atom with an atom of (negative) electricity, called an **electron**, and a positive ion like that of silver as the result of removing an atom of electricity, an electron, from an atom of silver. An atom of metallic silver is therefore regarded as a combination of electrons with an equivalent amount of positive electricity. In fact it is these electrons, free to move through the metal, that are supposed to explain the electric conductivity of metallic silver. As confirmation we may mention that metals which are good conductors, in which the electrons are held loosely, are the ones in general which are most easily changed to positive ions in solution. If we adopt the symbol $(-)$ to denote the electron, we may represent by equations such as the following what is supposed to happen when ions change into elements or into other ions, etc.:

$$Cu = Cu^{++} + 2(-),$$
$$Cl_2 + 2(-) = 2\,Cl^-,$$
$$Fe^{+++} + (-) = Fe^{++},$$
$$2\,OH^- = 2(-) + H_2O + \tfrac{1}{2}O_2.$$

Having presented evidence that electrolytes are dissociated into charged ions in dilute aqueous solution, and having found how their formulas should be written in order to express their electrical behavior, let us examine other properties of these solutions to see whether there is general confirmation of the conclusions thus far reached.

The Properties of Dilute Aqueous Solutions of Strong Electrolytes Are the Sum of Independent Sets of Properties, Hence Independent Substances Are Present. It is found that all of the properties of dilute solutions of strong electrolytes are the sum of independent sets of properties belonging to the different kinds of ions present. For example, the colors of salts of a colored with a colorless constituent may be different when the salts are in the solid state, but the color becomes the same when the substance is dissolved in a large amount of water. Solid $CuCl_2$, $CuBr_2$ and $Cu(NO_3)_2$ are colored green, brown and blue, respectively, but in dilute aqueous solution all assume the same greenish blue color. Since we recognize substances by their properties, we conclude that we have in solution the same substance. Again, the electrical conductivity, refractive index, density, etc., of these solutions depend only on the ions present, and not upon the substances giving the ions. If, say, 0.1 mol of NaCl and 0.1 mol of KNO_3 are dissolved together in a liter of water, the properties of the solution are the same as if the solution were made from 0.1 mol of KCl and 0.1 mol of $NaNO_3$ dissolved in the same amount of water.

Most striking of all, perhaps, are the chemical reactions. It is not possible to predict the properties of gaseous HCl from the properties of hydrogen and those of chlorine, but it is possible to predict the properties of a dilute aqueous solution of HCl from the properties common to all other acids, on the one hand, and those common to all soluble chlorides on the other hand. The hydrogen ion in this solution reacts in the same way and has the same properties as the hydrogen ion obtained from any other acid, as explained in Chapter V. It affects indicators in the same way, it reacts with carbonates, dissolves zinc, tastes sour, just as it always does unless the other ion present exerts some complicating effect on these tests. The chloride ion gives precipitates with the same reagents, such as $AgNO_3$ or $HgNO_3$ solutions, as are obtained from all other chloride electrolytes. Knowing the properties of chloride ion, as obtained from some chloride, and knowing the properties of some cation, say barium ion, we can predict the properties of dilute solutions of barium chloride, without the aid of direct experiment. This makes it possible to simplify enormously the labor of learning the chemical reactions of electrolytes upon each other. It is necessary only to know the reactions given by the important ions in order to predict the reactions of the enormous number of electrolytes which might be obtained by combinations of these ions. Instead of remembering the action of a large number of sulfates individually upon all soluble barium salts, it suffices to remember that barium ion, Ba^{++}, reacts with sulfate ion, SO_4^{--}, to give a very insoluble white precipitate of barium sulfate, $BaSO_4$. Such generalizations cannot be made with any degree of assurance with substances that are un-ionized. Alcohol and

phenol (carbolic acid) both contain the hydroxyl radical (OH), their formulas being C_2H_5OH and C_6H_5OH, respectively, but these are not appreciably ionized, and when dissolved in water react very differently, having no set of properties in common. Again, it is not correct to conclude that silver nitrate is a "test for chlorine," as is sometimes stated. A substance like chloroform, $CHCl_3$, will give no such test unless it is heated with silver nitrate for a long time. A solution of potassium chlorate gives no precipitate with silver ion, Ag^+, because, although it contains chlorine, it yields no chloride ion, Cl^-, but, instead, chlorate ion, ClO_3^-.

The value of the ionic theory is very great in reducing equations to their simplest terms and focusing the attention on the essential reactions taking place.

Heats of Reaction in Dilute Solutions of Strong Electrolytes Depend on the Reacting Ions Only. Heats of reaction between ions in dilute solution are independent of the nature of any other ions present. This is not true for substances not in solution. Solid NaOH and solid KOH do not give the same heat of neutralization with concentrated sulfuric or nitric acid, but when both acid and base are dilute, the amount of heat liberated is always the same, 13,700 calories per equivalent. Since the heat liberated is the same, the reaction liberating it is likely to be the same, and the ionic theory indicates that this should be the case. Instead of writing

$$NaOH + HCl = H_2O + NaCl$$

and

$$KOH + HNO_3 = H_2O + KNO_3$$

for the reactions in dilute solution, which would lead us to expect different heats of reaction, we should, according to previous evidence, write,

$$Na^+ + OH^- + H^+ + Cl^- = H_2O + Na^+ + Cl^- + 13{,}700 \text{ cal.}$$
$$K^+ + OH^- + H^+ + NO_3^- = H_2O + K^+ + NO_3^- + 13{,}700 \text{ cal.}$$

The ionic form of the equations indicates that nothing happens to anything except H^+ and OH^-, which unite to form H_2O; the other ions, being unaffected, may be canceled from the equation, leaving simply

$$H^+ + OH^- = H_2O + 13{,}700 \text{ cal.}$$

as the fundamental and only reaction in both cases.

The same would apply to precipitations. Any soluble barium salt would give the same heat effect per mol with any soluble sulfate, since, no matter what other ions are present in the solution, the essential reaction is

$$Ba^{++} + SO_4^{--} = BaSO_4 + 5600 \text{ cal.}$$

If, however, $Ba(OH)_2$ and H_2SO_4 solutions be used, the heat of reaction would, of course, be no longer the same as above, for then we would have occurring simultaneously two independent reactions, each with its own heat effect, and the ionic equation

$$Ba^{++} + 2\,OH^- + 2\,H^+ + SO_4^{--} = BaSO_4 + 2\,H_2O + 2 \times 13{,}700 \text{ cal.} + 5600 \text{ cal.}$$

shows that nothing should be canceled out.

The Degree of Ionization of Strong Electrolytes. We have seen the evidence that the substances we call strong electrolytes are highly ionized in aqueous solution, and we may ask the question: How completely does this dissociation

take place? The following table shows the fraction of the solute ionized (the " degree of ionization ") according to the evidence of conductivity and freezing point. In calculating from electrical conductivity the idea used is to compare the actual conductivity with that calculated on the assumption of complete ionization. We have not space to go into the explanation of this method. In interpreting the freezing point measurements the idea is to compare the actual lowering with that which would be expected if no ionization took place, and to calculate the increase in the number of mols due to dissociation from the abnormality in the freezing point lowering. It will be seen that the degree of ionization calculated by these two methods is fairly concordant. The differences are probably due, in part, to the fact that the law for the freezing point lowering is not an exact law and, in part, to ambiguity as to just how far apart the ions must be before they are to be considered dissociated. Some molecules pass for dissociated according to one method but not according to the other. For all practical qualitative purposes in predicting the results of chemical reactions, as will be done in later chapters, it suffices to consider these substances as completely ionized.

Substance	Fraction Ionized in 0.05 Molal Solution	
	By Freezing Point Lowering	By Electrical Conductivity
HCl	0.93	0.94
HNO_3	.91	.94
NaCl	.89	.88
KNO_3	.84	.88
Na_2SO_4	.74	.70
$CaCl_2$	.82	.76

Weak Acids and Bases Are Less Ionized than Strong Acids and Bases in Solutions of the Same Concentration. There are some acids and bases which show the properties of hydrogen and hydroxide ions, respectively, to a much less extent than do strong acids and bases in solutions of the same concentration. Solutions of HCl, HNO_3 and H_2SO_4, at the same concentration, say 0.01 normal, would have about the same sour taste, but 0.01 normal acetic acid, $HC_2H_3O_2$, would not taste nearly so sour. The first three acids would show almost identical colors with an indicator like methyl violet, sensitive to that degree of acidity, but it would require approximately normal acetic acid to show the same color. The same weakness on the part of acetic acid is shown in power to conduct current. While, therefore, the properties of acetic acid indicate that it yields hydrogen ion in water, they also indicate that only a little of the hydrogen of the acid is ionized. Again, while the effect of acetic acid on the freezing point of water is greater than that of an un-ionized substance like sugar, it is not double the latter, as is approximately the case with an acid like hydrochloric acid. Its heat of neutralization is no longer 13,700 cal., as with a strong acid, but has a different value, and includes the heat of dissociation of the acid during its neutralization.

There are a number of such weak acids, including carbonic acid, H_2CO_3, boric acid, H_3BO_3, hydrogen sulfide (hydrosulfuric acid), H_2S, silicic acid, H_2SiO_3 (also many poly-silicic acids), nitrous acid, HNO_2, arsenous acid, H_3AsO_3, arsenic acid, H_3AsO_4, phosphorous acid, H_3PO_3, hypophosphorous acid, H_3PO_2, hypochlorous acid, HClO, etc. They vary in strength considerably, as indicated by

the figures in the table on page 140 giving the degree of ionization or fraction ionized in 0.1 molal solution.

The most important weak base ordinarily encountered is ammonium hydroxide, NH_4OH. It is this quality which makes it useful in cleansing, for although it does not yield enough free hydroxide ion to be injurious in washing, yet, if the little it does yield is used up, more can dissociate, the undissociated portion acting as a sort of reserve for hydroxide ion.

Weak Salts. Most salts are highly ionized when in solution, even though they be salts of weak acids or bases, like sodium acetate or ammonium chloride. There are, however, a few exceptions, including lead acetate, $Pb(C_2H_3O_2)_2$, the halides of cadmium, $CdCl_2$, $CdBr_2$ and CdI_2, mercuric chloride, $HgCl_2$, mercuric cyanide, $Hg(CN)_2$, and ferric sulfocyanate, $Fe(CNS)_3$. These salts are poor electrolytes, and their reactions in solution show the presence of relatively few ions. For example, all ordinary soluble chlorides give a precipitate of lead chloride, $PbCl_2$, on the addition of lead ion to their solutions. With mercuric chloride, however, no precipitate is obtained, indicating that there is less chloride ion in a concentrated solution of mercuric chloride than in a saturated solution of the rather insoluble lead chloride. If, however, silver ion is taken, a precipitate is formed, for silver chloride, AgCl, is much less soluble than lead chloride, and $HgCl_2$ yields enough chloride ion to precipitate it.

Ionization of Weak Polybasic Acids in Steps. It is found that the two or more hydrogen atoms in the molecule of a polybasic acid like H_2CO_3, or H_2S or H_3PO_4, tend to dissociate with unequal readiness into ions. While the first hydrogen atom of H_2CO_3 is but slightly ionized, it is possible

to neutralize it with OH^-, forming water and HCO_3^-, before the neutralization of the second hydrogen atom, in the HCO_3^-, begins. This explains the ease with which it is possible to form acid salts in such cases. The first atom of hydrogen in H_3PO_4 ionizes readily, corresponding to a moderately strong acid, the second ionizes from $H_2PO_4^-$ with much less ease, so that the ion $H_2PO_4^-$ is a rather weak acid, while the third is hard to neutralize, HPO_4^{--} being a very weak acid. Conversely, when hydrogen ion, H^+, is added to an ion like PO_4^{---} it is taken up very completely at first until the latter is converted into HPO_4^{--}, then less completely until $H_2PO_4^-$ is formed, and then only a little to form H_3PO_4. It takes, likewise, a smaller concentration of H^+ to change CO_3^{--} to HCO_3^- than it does to change HCO_3^- to H_2CO_3.

IONIZATION OF WEAK ELECTROLYTES

	Fraction Ionized in 0.1 Molal Solution
Acetic acid, $HC_2H_3O_2$	0.013
Carbonic acid, H_2CO_3	0.0017
Dihydrogen phosphate ion, $H_2PO_4^-$	0.0014
Hydrogen sulfide, H_2S	0.001
Hydrocyanic acid, HCN	0.0001
Acid carbonate ion, HCO_3^-	0.00002
Monohydrogen phosphate ion, HPO_4^{--}	0.000002
Ammonium hydroxide, NH_4OH	0.017
Cadmium iodide, CdI_2	0.10
Mercuric chloride, $HgCl_2$	0.00006

Ionization in Other Solvents than Water. Water is the chief solvent in which we are interested, but there are others which can dissolve electrolytes with ionization. The most important of these are liquid ammonia and the alcohols. Ionization in all other solvents that have been investigated

is less than in water, and seems to be roughly proportioned to the dielectric constant of the liquid. The following values for the dielectric constants for several liquids are of interest in this connection:

Water	80	Ammonia	16
Methyl (wood) alcohol	31	Chloroform	5
Ethyl alcohol	26	Ether	4
Acetone	22		

Ionization of Fused Salts. Fused salts appear to be highly ionized, conducting the electric current very rapidly. Those most highly ionized are probably those in which there is the greatest difference in metallic character between the two constituent parts. On account of this high conductivity many substances are obtained industrially by the electrolysis of fused salts rather than of aqueous solutions. This is the case especially with metals like sodium, calcium and aluminum, where, instead of the desired metal, the hydrogen from the water would be deposited at the cathode. Sodium is obtained by the electrolysis of fused NaOH, when steam and oxygen are produced at the anode. Calcium is obtained, along with chlorine gas, by the electrolysis of fused calcium chloride. Aluminum, used at the present time in such large amounts, is obtained by the electrolysis of Al_2O_3 dissolved in fused cryolite, Na_3AlF_6.

Ionization of Water. Water itself is very slightly ionized. The purest water that can be prepared has a very slight conductivity due to H^+ and OH^-. Knowing the conductivities of these ions in more concentrated solution, as we do from measurements with acids and bases, it is possible to calculate the concentration of these ions in water to be approximately 10^{-7} molal at ordinary temperatures. This

corresponds to 0.1 milligram of H^+ and 1.7 milligrams of OH^- per ton of water. Other methods of measurement confirm these figures.

EXERCISES

1. How would you define acid, base, salt, in terms of the ionic theory?

2. Summarize in writing the evidence in favor of the theory of electrolytic dissociation.

3. State in writing all the evidence you have learned, showing that a solution of acetic acid is much less ionized than one of hydrochloric acid of the same concentration.

4. Divide the following substances into two lists, one for those slightly ionized in water, the other for those highly ionized: ammonium hydroxide, ammonium chloride, hydrochloric acid, sodium acetate, carbonic acid, sodium chloride, mercuric chloride.

5. Write the formulas of all the salts that can be formed from the following ions: Ca^{++}, Mg^{++}, Fe^{+++}, Al^{+++}, SO_4^{--}, Cl^-.

6. What are the properties of H_2 and H^+? How might each one be converted into the other?

7. What are the properties of the following substances: Cu; Cu^{++}; Ag; Ag^+; Cl_2; Cl^-?

8. Describe some of the properties of the dilute aqueous solutions of the following: HCl; KNO_3; H_2SO_4; Na_2SO_4; KCl; $CuCl_2$; $CuSO_4$.

9. How does the evidence obtained from the heat of neutralization support the ionic theory?

10. Write the principal reaction occurring when (*a*) NaCl dissolves in water; (*b*) a solution of sodium sulfate is evaporated; (*c*) when concentrated HCl solution is warmed.

11. In writing the following equations represent all substances by formulas indicating that they are mainly ionized or un-ionized, as the case may be: a solution of acetic acid is neutralized by one of sodium hydroxide; silver nitrate and potassium chloride solutions are mixed giving a precipitate of silver chloride; dilute hydrochloric acid acts on a solution of sodium carbonate giving CO_2 gas, water

and sodium chloride solution; zinc is put into a solution of copper sulfate, giving a precipitate of metallic copper; concentrated sulfuric acid acts on solid sodium chloride, giving hydrogen chloride gas and solid sodium sulfate; mercuric chloride solution is treated with hydrogen sulfide gas, giving a precipitate of mercuric sulfide, etc.

12. What is the concentration of OH^- in (*a*) equivalents per liter, and (*b*) grams per liter, when 1.48 g. of $Ca(OH)_2$ is dissolved in 500 cc.? *Ans.* (*a*) 0.08*N*; (*b*) 1.36 g. per liter.

13. What is the valence of each element in the following substances: Cu^{++}, Ag^+, OH^-, $Al(OH)_3$, Cl_2, Cl^-, $HgCl_2$, H_2S, NH_4^+, H_2O?

14. Define or explain the following terms: ion, electrolyte, degree of ionization, faraday, electron.

15. What is the degree of ionization of a weak monacid base if the concentration of the OH^- in a 0.5 normal solution is 0.002 normal? *Ans.* 0.004.

16. (*a*) What is the concentration of H^+ in a 2 normal solution of acetic acid if it is 0.006 ionized? (*b*) What is the concentration of Ac^- (*i.e.*, $C_2H_3O_2^-$)? (*c*) Of the un-ionized HAc?

Ans. (*a*) 0.012*N*; (*b*) 0.012*N*; (*c*) 1.988*N*.

17. How many (*a*) faradays, (*b*) coulombs are required to deposit 1 g. of each of the following ions at the appropriate electrode; and (*c*) how long will it take using a current of 1 ampere: (1) H^+, (2) Ni^{++}, (3) Cl^-, (4) Al^{+++}?

Ans. (*a*) (1) 1.00, (2) 0.0341, (3) 0.0282, (4) 0.112 faradays;
(*b*) (1) 96,540, (2) 3280, (3) 2720, (4) 10,700 coulombs;
(*c*) (1) 26 h. 49 min., (2) 54 min. 40 sec., (3) 45 min. 20 sec., (4) 2 h. 58 min. 20 sec.

CHAPTER XI

THE SPEED OF CHEMICAL REACTIONS

The previous chapters have been taken up with various aspects of the nature and composition of substances, and with the representation of substances and their reactions by means of formulas and equations. We are now ready to inquire into the means of controlling chemical reactions so as to realize desirable possibilities or prevent undesirable ones. There are two factors involved in this control, the direction and the speed. For example, at high temperatures the following reaction takes place readily:

$$2\ NH_3 = N_2 + 3\ H_2.$$

The theory to be developed in Chapter XV shows that it should be possible to reverse this reaction at low temperatures and make ammonia from its elements. We find by experiment, however, that the reaction proceeds so slowly at low temperatures as to be utterly useless as a means of making ammonia, and that we must seek some means for its acceleration in order to make it of any practical use. The means of altering the direction of a reaction will be discussed in the following chapters, this one being devoted to the question of speed in reactions, where the direction is already assured. Sometimes we may wish to increase the speed of a reaction, as in the cooking of food, and sometimes we may wish to retard an undesirable reaction, such

as the rusting of iron or the decay of wood. How may this be done?

Application of the Kinetic Theory. We have seen, in connection with the behavior of gases and solutions, Chapters II and IV, how fruitful is the kinetic theory of matter. We may apply it with equal success to the question of the means for controlling the speed of chemical reactions. In order that reactions may take place between different substances their molecules must come together, or collide. We should therefore expect any means of increasing the number (and perhaps the force) of these collisions to be effective in increasing the speed. What means are available for changing the number and speed of these collisions?

Effect of Temperature. Since the kinetic theory connects the temperature of any body with the velocity of the molecules composing it, one way indicated for increasing the number and also the force of the molecular collisions is to increase the temperature. We find, as a matter of fact, that the effect of increasing the temperature is always to increase the reaction velocity. For reactions occurring within a single phase, *e.g.*, between dissolved or gaseous substances, it is found that the effect of increasing the temperature 10° is usually to increase the speed between two and three times. Where the reaction occurs at the boundary line between two phases, as in dissolving a solid, the effect of temperature is usually somewhat less.

Chemists constantly make use of the accelerating effect of higher temperature in chemical reactions, and we see it constantly in everyday life. The reactions responsible for the growth of plants, for the decay of dead animal and plant substances, for the souring of milk, are all greatly influenced

by the temperature, so that the importance of warmth for growth and of cold storage for preservation is well known to all. The housewife sets her bread to rise in a warm place to hasten the fermentation which produces the carbon dioxide. Those who have lived or camped at high altitudes know of the difficulty of cooking certain foods at the lower temperature at which water boils under such conditions. The difficulty is sometimes solved by means of "pressure cookers," which hold the steam under pressure, allowing a higher temperature to be reached. Such an apparatus may also be used at ordinary altitudes, resulting in a great saving of fuel when cooking such things as beans or the tougher cuts of meat, for it requires scarcely any more fuel to maintain a temperature of 120° than it does to maintain one of 100°, although a reaction that requires 5 hours at the latter temperature might be completed in less than 1 hour at the former. In such processes as extracting glue, gelatin and fats "superheated steam" is used with similar effect. The speed of cooking such a thing as a potato is also increased by cutting it into small pieces, so that all parts of it are quickly brought to the temperature of the boiling water in which it is immersed.

The process of hardening steel is an interesting case of retarding a reaction by lowering the temperature. Above 725° a steel containing 0.9 per cent carbon consists of a hard, tough variety of iron holding the carbon in solid solution, but below that temperature it tends to change into a heterogeneous mixture, shown in Fig. 4, p. 9, of soft iron (like wrought iron) and a hard, brittle iron carbide, Fe_3C, known as cementite. However, this transition requires an appreciable time, and if the steel, heated above 725°, is

suddenly cooled by quenching in water, so that low temperatures are quickly reached, the tough solid solution may be obtained at ordinary temperatures, where the velocity of the change is practically negligible. This is shown in Fig. 1, p. 9. A solution which required 10 seconds for transition at 720° to the variety stable at ordinary temperatures would require 300,000 billion years at 20° if the reaction velocity were halved for every 10° fall in temperature. Hardened steel is thus an unstable substance at ordinary temperatures but we can keep it almost indefinitely by reason of the extreme slowness of its change into the stable variety. If we cool the steel slowly, *i.e.*, anneal it, or if we allow the hardened steel to get too warm for a while, as by too rapid grinding or cutting with a tool, it changes into the stable soft mixture, losing its " temper."

Many chemical substances are similarly unstable at ordinary temperatures, existing only because the speed at which they decompose is small. In this class are included ozone, O_3, hydrogen peroxide, H_2O_2, nitric oxide, NO, and all explosives. Nitric oxide is stable in the true sense only at the temperature of a very hot electric arc and it is obtained at ordinary temperatures by a process of rapid cooling similar in principle to the hardening of steel.

Spontaneous combustion is the result of the preliminary slow oxidation which many combustible substances undergo in contact with air. Ordinarily the heat of these reactions is liberated so slowly that it has time to be conducted away, so that no perceptible rise in temperature of the oxidizing material takes place. When, however, the material is a poor conductor of heat, like oil-soaked cotton waste, and is in large quantities, so that the heat produced is partly retained,

then the rise in temperature causes an increase in the rate of oxidation, with a further gradual rise in temperature, until the temperature of ordinary rapid combustion is attained, and the material bursts into flames.

Effect of Concentration. Another means of increasing the number of favorable collisions between molecules is to increase the concentration of the reacting substances. The more concentrated a reacting substance is, the more chances there are of its molecules colliding with those of other substances, hence an increase in the concentration of each kind of reacting molecule should increase the speed of reaction. If, for example, two molecules have to collide in order to bring about a certain reaction, then doubling the concentration of either should double the speed of reaction, and doubling the concentration of both should quadruple the speed. Of course, as the reacting substances are used up the speed diminishes.

Numerical Relation between Concentration and Speed. If c_1, c_2, c_3, etc., denote the concentrations of the reacting molecules, then the velocity of the reaction, v, as measured by the rate of disappearance of one of the substances or the formation of another, is proportional to, or equal to a constant times, the product of the concentration of the reacting molecules, *i.e.*, $v = kc_1c_2c_3 \cdots$. The so-called "order" of the reaction is the number of reacting molecules which determine its speed. If there is only one kind of molecule reacting, two of which have to collide to react, then $c_1 = c_2$, and $v = kc_1^2$. This would be called a reaction of the second order, or a bimolecular reaction. In a reaction like

$$2\,Fe^{+++} + Sn^{++} = 2\,Fe^{++} + Sn^{++++},$$

if we let c_1 denote the concentration of ferric ion, Fe^{+++}, and c_2 denote that of the stannous ion, Sn^{++}, we have as the expression for the velocity $v = kc_1^2c_2$. This would be a reaction of the third order, or a trimolecular reaction. When the reaction appears to take place between several molecules, we usually find it taking place in stages, since the chances of a large number of molecules colliding simultaneously are vastly less than for a few molecules. Thus, the equation for the burning of acetylene,

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O,$$

appears to depend on the collision of seven molecules, which would make it a reaction of the seventh order, but measurement shows it to be of the second order. Evidently there occur simultaneous reactions, a slower one, probably

$$C_2H_2 + O_2 = 2\,CO + H_2,$$

which determines the speed of the total reaction, and probably two more rapid reactions,

$$2\,CO + O_2 = 2\,CO_2, \text{ and } 2\,H_2 + O_2 = 2\,H_2O.$$

Measurements of the rate at which the speed falls off enable us to determine the order of the reaction and hence, often, to determine what steps occur in complicated reactions.

Effect of Stirring and of Contact Surface in Reactions Occurring at the Boundaries between Phases. If a reaction occurs at the boundary between phases, as in the solution of a solid in a liquid, it is evident that stirring would have great effect in bringing fresh reacting molecules to the surface of contact, also in removing the products of reaction from the scene of action. The natural tendency of the molecules to diffuse can thus be greatly aided.

Likewise, contact between the materials in the two phases can be aided by having the contact surface large. For this reason powdered sugar will dissolve more rapidly than granulated or lump sugar.

We may summarize and illustrate the foregoing by stating the conditions for the rapid solution of a metal in acid as follows: high temperature, concentrated acid (unless the salt produced would be thereby rendered insoluble, preventing its diffusion away from the surface of the metal), the use of a strong acid like hydrochloric acid, giving a high concentration of hydrogen ion, instead of a weak acid like acetic acid, giving a small concentration of hydrogen ion (assuming that the metal is a base metal which will be dissolved by hydrogen ion), stirring the solution, and using the metal in rather finely divided condition rather than in large pieces.

An undesirable reaction may, of course, be hindered by the converse of the above means.

Effect of Catalysts. Many reactions can be accelerated or retarded by the presence of substances which are not themselves permanently used up by the reaction, and which need be present only in small amount to affect the speed for a large amount of reacting mixture. Such substances are called **catalysts**. One class of catalysts acts by furnishing a surface at which the reacting molecules are condensed and concentrated, causing them to come into more intimate contact. Platinum and palladium act in this way for a number of gas reactions. Hydrogen and oxygen scarcely react at all at ordinary temperatures, but platinum and palladium have the power to absorb these gases, especially the hydrogen, and allow them to react with each other.

Under suitable conditions the heat produced by this union may be sufficient to raise the temperature of the metal to a point where it can ignite the remaining gas mixture. Some gas and cigar lighters are constructed on this principle, and when the platinum or palladium is held in the stream of gas mixed with air, or in the escaping vapors of wood alcohol from a wick, the gas or vapor is ignited by the heat generated at first in the catalyst. Platinum finds extensive use in the "contact process" for the manufacture of sulfuric acid. As will be explained in Chapter XIV, the reaction

$$2\,SO_2 + O_2 = 2\,SO_3$$

(sulfuric acid is obtained by dissolving SO_3 in water) occurs in the desired direction only at lower temperatures, where the reaction proceeds too slowly to be of use. When, however, the gases are passed over platinum at about 500° C. they react readily, so that the process has supplanted the older "lead-chamber process" to a considerable extent.

When platinum is used to catalyze reactions its effectiveness may be increased by increasing the surface as much as possible, since the reactions occur at the surface of the metal. This is particularly important because of the high cost of platinum. The usual form in which it is used is "platinized asbestos," made by wetting asbestos fiber with a solution of a platinum salt and then heating it so as to decompose the salt and yield finely divided metallic platinum.

The union of nitrogen and hydrogen directly to give ammonia, referred to at the beginning of this chapter, is brought about by the aid of a similar catalyst, uranium, to whose aid we owe this important means for the fixation of atmospheric nitrogen and its application as fertilizer.

Hydrogen peroxide is a very unstable substance, tending to decompose so as to give oxygen and water. This decomposition is aided by the presence of finely divided solids, such as manganese dioxide, MnO_2. This oxide likewise catalyzes other reactions where oxygen is evolved, notably

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

In making oxygen by heating potassium chlorate it is customary to add powdered manganese dioxide, so that the oxygen will be evolved more smoothly and at a lower temperature.

To prevent the decomposition of hydrogen peroxide, besides keeping it dilute and cool, as the kinetic theory would require, a negative or retarding catalyst is frequently added in the form of acetanilid, $C_6H_5NHOC_2H_3$.

Many catalysts evidently act as " carriers," by the formation of an intermediate product which then decomposes readily. Such a catalyst is NO, as used in the " lead-chamber process " for the manufacture of sulfuric acid. The reaction

$$SO_2 + H_2O + \tfrac{1}{2}\,O_2 = H_2SO_4$$

does not occur with sufficient speed, but since the reaction

$$NO + \tfrac{1}{2}\,O_2 = NO_2$$

occurs readily in both directions, the oxides of nitrogen make the oxygen available in the following way,

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO.$$

The NO_2 is regenerated as shown above, so that a little of it suffices for the manufacture of an almost indefinite quantity of sulfuric acid.

An interesting reaction is the " inversion " of cane sugar, which consists in its splitting up, with the addition of a

molecule of water, into two molecules of simpler sugars, fructose and glucose, containing the same atoms but in different arrangement. The reaction is

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 \text{ (glucose)} + C_6H_{12}O_6 \text{ (fructose)}.$$

The resulting mixture of sugars is often called invert sugar. This reaction is catalyzed by the hydrogen ion of acids and the speed of inversion is proportional to the concentration of hydrogen ion, which doubtless forms an intermediate product. Since the resulting invert sugar does not easily crystallize, and is, moreover, less sweet than the equivalent amount of cane sugar, it is important, in the refining of sugar, to avoid all acidity of the sugar solutions. When stewed fruit is sweetened the effect of the sugar will be greater if the fruit is first allowed to cool, retarding the inversion of the sugar by the acid of the fruit. The altered taste of lemonade that has stood for some hours is due mainly to this inversion of its sugar. It is of interest to note that the sugar in honey is invert sugar. The inversion doubtless takes place in the body of the bee when it is gathered, and prevents subsequent crystallization in the comb.

By a process analogous to the inversion of sugar, starch may be made to take up water, becoming transformed into a mixture of various sugars to which is given the commercial name "glucose." Large quantities of syrup and sugar are made from cornstarch by digestion with acid, which acts as the catalyst.

Water is a catalyst for many reactions. Absolutely dry CO will not burn. Dry $AgNO_3$ and HCl dissolved in ether form no precipitate of AgCl. When ordinary NH_4Cl is heated it sublimes, dissociating into NH_3 and HCl gases.

If, however, the salt is quite dry, it vaporizes without dissociation.

Enzymes. An important class of catalysts, known as enzymes, are produced by living organisms and catalyze many reactions. The ptyalin of saliva, whose function is to convert starch into sugar, the diastase of malt, which has a similar action, and the zymase of the yeast plant, which converts certain sugars into alcohol and carbon dioxide, are examples of important enzymes. Similar bodies are thought to play fundamental rôles in the processes of growth and nutrition of plants and animals.

EXERCISES

1. Define catalyst.

2. Divide the catalysts mentioned in the text into surface catalysts and dissolved catalysts.

3. What effect may a double boiler have on the speed of cooking food?

4. What means could you employ for rapidly washing photographic prints free from the "hypo" of the fixing bath?

5. How might you alter the time required for developing a photographic negative?

6. How might you endeavor to increase the speed of the reaction:

$$BrO_3^- + 6\ I^- + 6\ H^+ = 3\ H_2O + Br^- + 3\ I_2?$$

What effect would acetic acid have upon the speed as compared with hydrochloric acid of the same concentration?

7. The organism existing in "mother of vinegar" converts alcohol into acetic acid by the reaction

$$C_2H_5OH + O_2 = C_2H_4O_2 + H_2O.$$

By what means could the manufacture of vinegar be hastened?

Thursday

CHAPTER XII

CHEMICAL EQUILIBRIUM. THE EFFECT OF CONCENTRATION

Reversibility of Chemical Reactions. The problem of the control of chemical reactions involves not only the speed, as discussed in Chapter XI, but also the fact that most reactions are reversible. We have, therefore, two problems as distinct from each other as are the speed and destination of a train. To reach a desired destination it is not sufficient to get on a fast train, the train must also move in the right direction. With chemical reactions, similarly, the conditions accelerating the reaction often alter the direction at the same time. For example, the velocity of formation of SO_3 from SO_2 and O_2 increases with the temperature, but the velocity of decomposition of SO_3 back into SO_2 and O_2 is likewise increased thereby, and more rapidly than the velocity of its formation, so that SO_3 becomes increasingly unstable at higher temperatures. Therefore, assuming that all the time necessary for them to take place is allowed, we will turn our attention to the problem of the direction of chemical reactions. Finally, in Chapter XIV, we will consider both effects together.

Most chemical reactions are reversible, that is, the products of a reaction may usually be made to react with each other to produce the original substances by suitable choice of

conditions. Many examples of this may be given. A liquid may be made to evaporate by raising the temperature or by reducing the pressure, and its vapor, conversely, may be recondensed to liquid by lowering the temperature or increasing the pressure. Solids may be liquefied by increasing the temperature, and liquids may be solidified by lowering the temperature. Gases may either be dissolved in liquids or driven out of solution by suitable changes in pressure or temperature. The naturally occurring mineral, gypsum, $CaSO_4 \cdot 2\,H_2O$, may be deprived of part of its water by moderate heating, giving plaster of Paris, which is approximately $CaSO_4 \cdot \frac{1}{2}\,H_2O$. When this is mixed with water the original dihydrate is re-formed, which causes the plaster to "set," due to the interlocking of the growing crystals of $CaSO_4 \cdot 2\,H_2O$. Nitric oxide, NO, is decomposed by gentle heating into nitrogen and oxygen, and yet, at the high temperature of the electric arc a considerable amount of nitric oxide may be formed from the nitrogen and oxygen of air. Oxygen, O_2, is changed into ozone, O_3, by the silent electric discharge, and then gradually reverts to oxygen again. When a lead storage battery is discharged the lead dioxide of the positive plate, the lead of the negative plate and the sulfuric acid in the solution react as follows:

$$PbO_2 + Pb + 4\,H^+ + 2\,SO_4^{--} = 2\,PbSO_4 + 2\,H_2O,$$

and when the battery is recharged the reverse reaction takes place, corresponding to the equation as read from right to left. When water charged with carbon dioxide passes over limestone rock, the following reaction occurs:

$$CaCO_3 + H_2O + CO_2 = Ca^{++} + 2\,HCO_3^-.$$

The calcium ion dissolved in the water produces what is called " hard water," and interferes with the cleansing power of soap by precipitating insoluble calcium soap. When this water is boiled, however, the CO_2 is driven off, and the calcium carbonate is re-precipitated, corresponding to the equation as read from right to left. When steam is passed through a tube containing iron filings or nails, heated to dull redness, the following reaction occurs:

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2.$$

When hydrogen is passed over the iron oxide, Fe_3O_4, under similar conditions, some of it is changed to steam with the reduction of the oxide to iron, exactly the reverse of the above. Illustrations of reversibility might be multiplied ad libitum.

The experimental proof of reversibility consists simply in mixing each set of substances, as indicated by the two sides of the equation, and seeking conditions under which the other set will be formed. The disappearance of any of the substances taken, or the appearance of any of the products, is usually sufficient proof that a reaction has taken place. What particular substance to test for is determined by the ease and decisiveness of the available tests. Thus the oxidation of mercury, represented by the equation,

$$2\ Hg + O_2 = 2\ HgO,$$

could be proved if conditions could be found under which mercury in contact with oxygen would increase in weight. A change in appearance corresponding to the red color of the oxide, or a decrease in the amount of the gaseous oxygen would suffice equally well. The reverse reaction, the dis-

sociation of mercuric oxide into mercury and oxygen, could be proved by taking the red mercuric oxide and discovering conditions of pressure and temperature under which there could be detected either the appearance of mercury or oxygen, or else a loss in weight.

It is frequently desirable to express in the equation for a reaction the fact that the reaction is reversible. This is done by substituting a double arrow, $\rightleftarrows$, for the equality sign. Written in this way, an equation such as the last above would appear as follows:

$$2\,Hg + O_2 \rightleftarrows 2\,HgO.$$

It must be remembered that the double arrow sign retains the full significance of the usual equality sign, merely adding further information, so that we would do well to regard it as an abbreviation for a fuller representation such as the following:

$$2\,Hg + O_2 \underset{\leftarrow}{\overset{\rightarrow}{=}} 2\,HgO.$$

Since nearly all reactions are reversible, however, the double arrow sign is in reality somewhat superfluous, except, perhaps, where it is desired to emphasize the fact of reversibility. Its absence must never be construed as indicating irreversibility. In view of these facts we will not ordinarily use it in the following pages.

It Is Possible to Have All of the Substances Involved in Reversible Reactions Present Together in Chemical Equilibrium with Each Other. Instead of passing steam over heated iron in a tube, as in the experiment described above, we might simply heat them together in a closed vessel. We would expect, as before, the formation of some hydrogen and iron oxide, corresponding to the equation as read

from left to right. Likewise, if we heat hydrogen and iron oxide together at the same temperature and in a similar vessel, we would expect the formation of iron and steam, corresponding to the equation as read from right to left. If we allow sufficient time for reaction in both cases how will the final state of affairs in one vessel compare with that in the other? It is obviously absurd to expect either reaction to go to completion, just as it would be absurd to expect a ball placed on a certain table to roll all the way from *a* to *b* when we have previously found that, when placed at *b*, it rolls towards *a*. Obviously there must be some intermediate position on the table at which it tends to come to rest no matter at which end it is started. Again, if it is found that one body becomes cooler when brought into a certain room, and another becomes warmer when brought into the same room, it is evident that each body will come eventually to the same temperature, that of the room, which must lie somewhere between the initial temperatures of the two bodies. By the same kind of reasoning, it should make no difference whether we start with $3\ Fe + 4\ H_2O$, or with $Fe_3O_4 + 4\ H_2$, if we heat them to a temperature at which they are able to react, in identical vessels, we will eventually get a mixture of all four substances in **chemical equilibrium.** The term "chemical equilibrium" signifies an adjustment of the amounts of the reacting substances, such that there is no further tendency to react, just as in "mechanical equilibrium" we have an adjustment of forces such that no further action takes place. This adjustment of the amounts of substances in chemical equilibrium may be thought of as the result of an adjustment between chemical forces. Just as a balance loaded with certain weights will finally come to rest,

provided that the balance is free to swing, at a position dependent only upon the weights on the pans and not upon the direction in which an original displacement took place, so in a reversible chemical reaction, the final equilibrium between the amounts of the reacting substances, provided that they are free to react (suitable temperature, catalyst, etc.), will depend only on the relative amounts of the substances present, and not upon which particular set of substances, as represented by the two sides of the equation, is chosen. There is, of course, no oscillation in reaching chemical equilibrium comparable to that of a balance in coming to rest.)

From a kinetic standpoint chemical equilibrium must be regarded as the result of two opposite reactions proceeding with equal speed. When, for example, we start with iron and steam, at a sufficiently high temperature, they react with a velocity depending on the concentration of steam molecules and on the surface of the iron. As these are used up the reaction gradually becomes slower. At the same time, as more hydrogen and iron oxide are produced, they begin to react with each other to regenerate the oxide and steam, with an increasing velocity, until the rate of one reaction just equals that of the other. This conception of equilibrium was used in connection with simpler phenomena in Chapter II, and has an important bearing on what is here to follow.

The Effect on Chemical Equilibrium of Changing the Concentration of the Reacting Substances. If a little weight is added to or taken from one pan of a balance in equilibrium, the pointer swings a little to one side or the other until a new position of equilibrium is reached. Similarly, when a chemical equilibrium exists, it is possible to disturb

it by any means which changes the relative speeds of the two opposing reactions. These rates may be affected by changing the temperature, or the total pressure on the reacting system, or the concentration of the substances involved. The effect of changing the temperature or total pressure will be discussed in Chapter XIV, and we will turn our attention first to changes in concentration.

If we recall the kinetic conception of chemical equilibrium, we will see that if we increase the concentration of one of the reacting substances, there are then more molecules of that substance present in a given space, so that their ability to find and react with other molecules is increased. This will cause a temporary gain in the rate of the reaction using up this kind of molecule, until more of the products of this reaction, represented on the other side of the equation, are produced, so as to equalize again the rates of the two reactions. The net result is that the reaction proceeds to some extent in the direction which will use up the substance whose concentration is thus increased.

For illustration let us consider a closed vessel containing SO_3, SO_2 and O_2 in chemical equilibrium, to attain which requires a sufficiently high temperature and perhaps a catalyst. When equilibrium is attained we must imagine that the two reactions, represented by the equation

$$2\,SO_2 + O_2 = 2\,SO_3,$$

read in both directions, are taking place with equal velocities, with a net result of no change in the relative amounts of the three gases present. Suppose, now, that more oxygen is introduced into the vessel. The increased number of oxygen molecules will render it easier for them

to collide with sulfur dioxide molecules, resulting in a more rapid formation of sulfur trioxide molecules. As the number of the latter increase their own speed of decomposition will increase until the two reactions again take place at equal rates. The net effect of this increase in the amount of oxygen is to cause more of it to be used up, with a decrease in the amount of sulfur dioxide and an increase in the amount of sulfur trioxide. The effect of adding or removing any of the three substances present can be predicted on the above basis.

From a technical point of view, in making sulfur trioxide, the important thing is to use up the sulfur dioxide as completely as possible, since the latter costs money, whereas the supply of oxygen is free. To accomplish this the kinetic theory indicates that it is desirable to have the oxygen in excess, since otherwise considerable sulfur dioxide would remain uncombined when equilibrium has been reached.

In general, after equilibrium has been reached, **the effect of any change in the concentration of the reacting substances is to cause that reaction to take place which neutralizes the effect of the change**; that is, if the concentration of any substance is increased, that reaction tends to take place which uses up that substance, and where the concentration of any substance is decreased, that reaction tends to take place which will replace that substance. This conclusion is a special case of a more general one, called the **Theorem of Le Chatelier**, which states that when equilibrium has been reached a change in *any* of the factors affecting equilibrium tends to make that reaction take place which will neutralize the effect of the change. The discussion of other factors will be taken up in Chapter XIV.

The above conclusion, in so far as concentration alone is concerned, is called the "Law of Mass Action," or the "Mass Law." This name is slightly misleading, since it is not the masses of the substances present, but their concentrations, or masses per unit volume, which determine equilibrium. This point was discussed in Chapter II, where it was shown that the depth of the water in equilibrium with its vapor, or the extent of the surface between the two phases, has no effect upon the equilibrium. On the other hand, a change in the concentration of the vapor, as by changing its volume, or in the concentration of the liquid, as by adding some other substance to it, *would* cause some reaction to take place. Likewise, in the equilibrium discussed above, between iron, its oxide, steam and hydrogen, the relative amounts of the solids have no more effect than would the addition of more salt to a saturated salt solution. The reaction takes place where the three phases, the two solids and the gas phase, are in contact, and its rate does not depend on the excess of either solid.

These same conclusions apply to reactions occurring in solution, including those between ionized substances. For example, that the reaction

$$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$$

will take place as read from left to right may be shown by taking pure acetic acid (which is un-ionized, as shown by its being a non-conductor) and dissolving it in water, when the solution will have the properties of hydrogen ion. That the reaction will also take place as read from right to left, may be shown by mixing a solution of a strong acid, like hydrochloric acid, giving a large concentration of hydrogen

ion, with one of sodium acetate, which gives a large concentration of acetate ion. We find that hydrogen ion disappears partly from the solution, and also that acetic acid appears, as is evident by its odor. It makes no difference, therefore, whether we start with a mol of acetic acid in a liter of water, or with a mol each of hydrogen and acetate ions in a liter of water, the final state of affairs is the same, which is that we will have present about 0.01 mol of each of the two ions and 0.99 mol of the undissociated molecule. If, subsequently, we add another mol of acetate ion (in solution with, say, sodium ion, which affects none of the substances present) some of the acetate ion will be able to use up more of the hydrogen ion, becoming acetic acid, resulting in a considerable decrease in the acidity (hydrogen ion concentration) of the solution. In like manner, solutions of the weak base ammonium hydroxide, NH_4OH, are much less alkaline in the presence of any substance which dissolves to yield an excess of ammonium ion, NH_4^+.

When experiment shows that one set of substances reacts almost completely to give certain products, then it must be evident that these products themselves, when mixed under the same conditions, will give but little of the original substances at equilibrium. When, for example, we have found that carbonic acid is extremely weak, dissociating but slightly according to the equation:

$$H_2CO_3 = H^+ + HCO_3^-,$$

then we should be able to conclude at once that when the ions are mixed, as in mixing hydrochloric acid and sodium acid carbonate solutions, they will unite almost completely to form carbonic acid.

Quantitative Expression of the Mass Law. In the above discussion of the effect of concentration on chemical equilibrium we have been content with predicting the direction of the effect of altering concentration, the qualitative effect, without inquiring how much a given equilibrium would be disturbed by a certain change in concentration of one or more of the reacting substances. This would be called the quantitative effect. Although the qualitative prediction suffices in most cases, it is nevertheless often desirable to make a quantitative prediction. This is possible by combining the quantitative expression for the speed of a chemical reaction, given in Chapter XI, with the idea introduced in this chapter, that at equilibrium the two opposite reactions are proceeding with equal velocity. For the sulfur trioxide reaction discussed above, we would have for the velocity of formation $v_1 = k_1 c^2_{SO_2} \cdot c_{O_2}$, where k_1 is a constant. Similarly, for the decomposition of the trioxide back into the dioxide and oxygen, we would have for the velocity $v_2 = k_2 c^2_{SO_3}$. At equilibrium the two velocities are equal, so that $k_1 c^2_{SO_2} \cdot c_{O_2} = k_2 c^2_{SO_3}$. Since k_1 and k_2 are constants their quotient is a constant, K, so that we may write

$$\frac{c^2_{SO_2} c_{O_2}}{c^2_{SO_3}} = K.$$

By means of this expression we are able to make qualitative as well as quantitative predictions. Since K is constant at a given temperature, the values of the three concentrations must always adjust themselves accordingly. For example, suppose that it were found by measurement, at a certain temperature, that when equilibrium was reached the concentrations were as follows: SO_2, 3 mols per liter,

O_2, 1 mol per liter, SO_3, 2 mols per liter. By substituting these values in the above expression we obtain for the value of the constant K, 2.25. From this we can calculate another set of equilibrium concentrations. Thus, if the concentration of O_2 were 5 mols per liter, and that of SO_3 2 mols per liter, we would have

$$\frac{c^2_{SO_2} \times 5}{4} = 2.25,$$

from which we would find the concentration of SO_2 in equilibrium with sulfur trioxide and oxygen at the new concentrations to be 1.34 mols per liter.

It is also the custom to denote concentrations by the formula of the substance inclosed in brackets or parenthesis. Using this notation we would write the above expression

$$\frac{(SO_2)^2(O_2)}{(SO_3)^2} = K,$$

which has exactly the same significance as before when c was used to denote concentration.

It may be worth while to give examples of the equilibrium equation for several other reactions.

Reaction	Equilibrium Equation
$N_2 + O_2 = 2\,NO$	$\frac{(NO)^2}{(N_2)(O_2)} = K$
$N_2 + 3\,H_2 = 2\,NH_3$	$\frac{(NH_3)^2}{(N_2)(H_2)^3} = K$
$CO_2 + C$ (solid) $= 2\,CO$	$\frac{(CO)^2}{(CO_2)} = K$

(Since carbon is solid its concentration is constant and need not be expressed in the equilibrium equation.)

$$Fe_3O_4 \text{ (solid)} + 4\,H_2 = 3\,Fe \text{ (solid)} + 4\,H_2O \qquad \frac{(H_2O)^4}{(H_2)^4} = K'$$

$$\text{or } \frac{(H_2O)}{(H_2)} = K$$

$$H^+ + C_2H_3O_2^- = HC_2H_3O_2 \qquad \frac{(H^+)(C_2H_3O_2^-)}{(HC_2H_3O_2)} = K$$

$$H^+ + HCO_3^- = H_2CO_3 \qquad \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = K$$

$$H^+ + CO_3^{--} = HCO_3^- \qquad \frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = K$$

Since the partial pressure of a gas is proportional to the number of molecules in a given space, and hence to the concentration, it is possible, where gases are concerned, to write partial pressures instead of concentrations, and have constant a similar function of partial pressures. This constant is not necessarily the same as that where concentrations are used, so that we will express it as K_p. We would write, accordingly,

$$\frac{p^2_{NO}}{p_{N_2} \cdot p_{O_2}} = K_p, \qquad \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} = K_p, \text{ etc.}$$

Dissociation Constants of Electrolytes. The equilibrium constants for the dissociation of an electrolyte, as with acetic and carbonic acids above, are often called **dissociation constants** or **ionization constants**, and express the strength of an acid or base in the most general way. It is evident that the stronger the electrolyte the larger are the concentrations written in the numerator of the fraction, hence the larger the dissociation constant. Instead of stating the degree of dissociation for an electrolyte at a certain concentration, as was done in Chapter X, page 140, it is more satisfactory to give the dissociation constant, from which the

degree of dissociation at any concentration may be calculated. The following values for certain familiar substances may be given:

Substance	Reaction	Dissociation Constant at Room Temperature
Acetic acid	$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$	1.8×10^{-5}
Dihydrogen phosphate ion	$H_2PO_4^- = H^+ + HPO_4^{--}$	2×10^{-7}
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	3×10^{-7}
Hydrogen sulfide	$H_2S = H^+ + HS^-$	10^{-7}
Hydrocyanic acid	$HCN = H^+ + CN^-$	10^{-9}
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{--}$	4×10^{-11}
Hydrosulfide ion	$HS^- = H^+ + S^{--}$	10^{-15}
Ammonium hydroxide	$NH_4OH = NH_4^+ + OH^-$	2.3×10^{-5}

The concentration of hydrogen ion in a solution of acetic acid, for example, may be calculated from the dissociation constant of the acid as follows: If the acid alone is present in the solution, the hydrogen ion and the acetate ion are at the same concentration, hence $(H^+) = (C_2H_3O_2^-)$. Suppose that the total concentration of acetic acid is 0.1 molal. The amount ionizing is so slight that the un-ionized acid may be considered as 0.1 molal without appreciable error, *i.e.*, $(HC_2H_3O_2) = 0.1$. Substituting these values in the equilibrium equation, we obtain

$$\frac{(H^+)^2}{0.1} = 1.8 \times 10^{-5}, \text{ and hence } (H^+) = 0.0013.$$

Again, suppose that 0.05 molal acetate ion is present in the same solution, then $(C_2H_3O_2^-) = 0.05$, $HC_2H_3O_2) = 0.1$ and $(H^+) = 0.000036$. It will be observed that the acidity of this solution is vastly less than that of the former.

Strong electrolytes do not obey the Mass Law, for reasons which there is not space here to discuss, so that calculations such as the above cannot be made with them. However,

little is lost on this account, as they may be considered, with sufficient accuracy for most purposes, as completely dissociated.

Chemical Equations Do Not Indicate Amounts Present at Equilibrium. It must be remembered, as was pointed out in Chapter III, that a chemical equation does not indicate that the reaction it represents will actually take place, and says nothing about the necessary conditions. When we write the equation

$$2\,SO_2 + O_2 = 2\,SO_3,$$

we should not read it "sulfur dioxide reacts with oxygen, etc.," but rather, *if* sulfur dioxide and oxygen can be made to react to form sulfur trioxide, they will do so in certain proportions by weight (expressed in mols or grams) and volume (if the temperature is such that they are in the gaseous state). As a matter of fact, in order to convert 1 mol of sulfur dioxide into sulfur trioxide in any reasonable time several things are necessary which are not indicated by the equation. The proper temperature is required, a catalyst must be used and an excess of both sulfur dioxide and oxygen must be present. In reactions which do not naturally run to completion, but which reach equilibrium with considerable amounts of all the substances still present, an excess of one or more of the reacting substances must be taken in order to get the desired amount of product, and *this excess is in no way indicated by the equation,* nor does the presence of this excess change the proportions in which the substances react.

We may illustrate this important point by imagining a Western celebration in which a large number of cowboys

are to ride wild horses. Now in order to have fifty mounted cowboys it would be necessary to have more than fifty cowboys and fifty horses present, for we will assume that cowboys are constantly being unhorsed. It might be necessary to have, say, seventy cowboys in order to have all the horses mounted most of the time. This does not affect the fundamental reversible reaction, which is

$$\text{Man} + \text{Horse} \rightleftarrows \text{Mounted horseman.}$$

If the men are in excess of the horses we will not have two men trying to ride one horse, nor, if the horses are in excess, will one man try to ride two horses. After equilibrium has been reached, in which there are, on the average, a certain number of each of the three varieties represented by the equation, if more men arrive, the reaction corresponding to the equation as read from left to right will take place in a few more cases, shifting the equilibrium so as to use up riderless horses, while if some of the unmounted men leave for the nearest saloon, the net result will be that the reaction as read from right to left will take place until a new condition of equilibrium is reached. Again, starting with sixty horses, in order to get fifty horsemen it might be necessary to have several hundred men, if bank-clerks were substituted for cowboys.

In analogous fashion, it would require more than 1 mol of H_2S in order to precipitate 1 mol of Cd^{++} as CdS by the reaction

$$Cd^{++} + H_2S = CdS + 2\,H^+.$$

Though the amounts reacting do so in the proportion indicated by the equation, an excess of both Cd^{++} and H_2S have to be present in order to make these amounts react.

If, instead of Cd^{++} we take Zn^{++}, we find that a still larger excess of H_2S must be present in order to produce 1 mol of sulfide. In either case, after equilibrium has been reached, it may be shifted so as to dissolve sulfide, either by the addition of more H^+, or by the removal of H_2S, as by boiling the mixture; or it might, on the other hand, be shifted so as to precipitate more of the Cd^{++}, if H_2S were added at a greater partial pressure (or concentration), or if H^+ were removed, as by the addition of OH^- or $C_2H_3O_2^-$.

EXERCISES

1. Describe experiments which would prove whether or not the following reactions can be made to take place in both directions:

$$2\ BaO\ (solid) + O_2 = 2\ BaO_2\ (solid);$$
$$H_2 + S\ (liquid) = H_2S;$$
$$Mg^{++} + 2\ NH_4OH = Mg(OH)_2\ (precipitate) + 2\ NH_4^+;$$
$$2\ CrO_4^{--}\ (yellow) + 2\ H^+ = H_2O + Cr_2O_7^{--}\ (red);$$
$$NH_4^+ + Cl^- + H_2O = NH_4OH + H^+ + Cl^-.$$

2. Hard water may be softened by means of an insoluble substance called by the commercial name, "permutite," $Na(H_6AlSiO_7)$, which exchanges the calcium (or magnesium) ion in the water for sodium ion as follows:

$$Ca^{++} + 2\ Na(H_6AlSiO_7)\ (solid) = 2\ Na^+ + Ca(H_6AlSiO_7)_2\ (solid).$$

Can you suggest a way of restoring the sodium permutite after it has all been changed to calcium or magnesium permutite?

3. Describe in words the effect of adding solid sodium acetate to a solution of acetic acid, and write an equation for the reaction.

4. The precipitation of manganese ion as manganese sulfide, according to the equation,

$$Mn^{++} + H_2S\ (gas) = MnS + 2\ H^+,$$

is never complete. How would you make the amount precipitated as great as possible? How would you redissolve all of the precipitate?

5. Write equations showing what happens when

(*a*) 2 mols of hydrogen are mixed with 4 mols of oxygen and an electric spark passed;

(*b*) dilute solutions containing respectively 1 mol of hydrochloric acid and 2 mols of sodium acetate are mixed.

6. (*a*) Which solution tastes more sour, vinegar or plain soda water?

(*b*) Which, then, of the two following reactions takes place more completely, as read from left to right:

$$HC_2H_3O_2 = H^+ + C_2H_3O_2^-, \text{ or } H_2CO_3 = H^+ + HCO_3^-?$$

(*c*) Which of the following reactions would yield the greater concentration of OH^-,

$$HCO_3^- + H_2O = H_2CO_3 + OH^-,$$

or

$$C_2H_3O_2^- + H_2O = HC_2H_3O_2 + OH^-?$$

7. Using the equilibrium constants given on page 168, calculate the (H^+) for acids and the (OH^-) for bases when the substance is present in 0.05 molal solution.

CHAPTER XIII

CHEMICAL EQUILIBRIUM. PROPERTIES WHICH MAY AFFECT CONCENTRATION

We have seen, in Chapter XII, that it is possible to control reactions which come to equilibrium by changing the concentrations of the reacting substances. A reaction may be made more complete by using the reacting substances at greater concentration, or by removing one or more of the products of the reaction. We may now ask the questions: In what ways may substances be added to or taken away from reacting mixtures, and what properties of substances determine whether a reaction proceeds more completely in one direction or another? The ability to answer these questions enables one, without previous experiment, to predict and control reactions in a large number of cases. It is important that the amount of experimental material to be memorized should be the minimum necessary to deal with the vast number of reactions likely to be encountered. How this material may be arranged and applied will be shown in the following pages.

Volatility. One of the properties of substances that may be utilized in bringing about reactions is volatility. If a certain reacting mixture is in an inclosed space, equilibrium may be reached long before all of the desired products are obtained; but if one of the substances produced is volatile

at the temperature of the reaction, it may be allowed to escape, or be pumped off, and its removal will allow more of it to be formed, according to the principle set forth in the last chapter. If this removal is continued, it may be possible to make the reaction go to completion. For example, if solutions of sodium chloride and sulfuric acid are mixed, there is only a small tendency to form hydrochloric acid, since the latter is a little stronger than the former. However, since hydrogen chloride, in the absence of water, is a gas, it is possible to produce it by the reaction between *solid* sodium chloride and *concentrated* sulfuric acid, as follows:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

If this were done in a closed vessel, equilibrium would be reached before much of the salt and sulfuric acid had reacted in this way; but if the vessel is open, so that the HCl gas can escape, then it can all be removed, and the reaction may go to completion. Further heating, if enough salt is present, will give neutral sodium sulfate, Na_2SO_4, the second step being

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The more volatile acid is thus driven out of its salt by the less volatile one. This principle is used in the manufacture of hydrochloric acid, where the gas is caught and dissolved in water. A number of other acids are obtained commercially from their salts by heating them with sulfuric acid in the same way, among them nitric acid, HNO_3, from the naturally occurring $NaNO_3$; hydrofluoric acid, H_2F_2, from fluorspar, CaF_2; acetic acid from calcium acetate,* etc.

* When wood is distilled the acetic acid is separated from the wood alcohol, acetone, etc., occurring in the distillate, by using slaked lime, $Ca(OH)_2$, in order to convert it into the non-volatile calcium acetate.

Sodium sulfate, on the other hand, may be changed to sodium phosphate by using P_2O_5, which is less volatile than SO_3. The reaction is

$$3\ Na_2SO_4 + P_2O_5 = 2\ Na_3PO_4 + 3\ SO_3.$$

This is a case where it may be more satisfactory to consider the salts as combinations of the metallic and non-metallic oxides, as explained in Chapter V. The equation is

$$3\ Na_2O \cdot SO_3 + P_2O_5 = (Na_2O)_3 \cdot P_2O_5 + 3\ SO_3.$$

Again, since SiO_2 is still less volatile than P_2O_5, a phosphate may be changed to a silicate by heating it to a sufficiently high temperature with SiO_2, as follows:

$$(Na_2O)_3 \cdot P_2O_5 + 3\ SiO_2 = 3\ Na_2O \cdot SiO_2 + P_2O_5.$$

In solution, where the difference in volatility of the above substances would not be evident, the reverse changes only would take place, since silicic, phosphoric and sulfuric acids are successively stronger, as will be explained presently.

It is well to remember that ammonium salts are easily volatilized, and that many chlorides are rather volatile, especially $HgCl_2$, $FeCl_3$, $AlCl_3$, $SbCl_3$, $SbCl_5$, $AsCl_3$, $SnCl_4$.

Solubility. The solubilities of substances have an important bearing on the course of reactions. When a rather insoluble salt is put into water a little of it dissolves, for almost no salts are so insoluble that the amount going into solution cannot be measured. The small quantity which does dissolve will be ionized, since nearly all salts are ionized in so far as they will go into solution. The equation expressing the reaction when such a salt is put into water should express this ionization, as exemplified by the following:

$$BaSO_4 \text{ (solid)} = Ba^{++} + SO_4^{--},$$
$$AgCl \text{ (solid)} = Ag^{+} + Cl^{-},$$
$$CaCO_3 \text{ (solid)} = Ca^{++} + CO_3^{--},$$
$$PbCrO_4 \text{ (solid)} = Pb^{++} + CrO_4^{--}.$$

When the solution is saturated there will be equilibrium between the solid salt, represented on the left side of each equation, and its ions in solution, represented on the right. The observed fact that all the above salts are only very slightly soluble means that the solutions will contain but very little of their ions. It also enables us to predict that if we mix the ions of any of the salts at any considerable concentration, they will react almost completely to form a **precipitate** (from a Latin word meaning to throw down) of the corresponding salt. A knowledge of the solubilities of salts, therefore, enables us to tell what ions will precipitate each other from solution. No matter what other ions are present, no matter from what compounds they are obtained, in any appreciable concentration Ba^{++} and SO_4^{--} will always form a precipitate of $BaSO_4$. Moreover, if it is desired to remove Ba^{++} from solution most completely, our knowledge of equilibrium indicates that we should add an excess of SO_4^{--}. This effect is constantly sought in quantitative analysis.

Conversely, if we wish to dissolve a precipitate, we must endeavor to remove from the solution one of its ions. This removal, in the case of ions, is not so simple as is the removal of a gas, but requires a knowledge of other combinations the ion is capable of forming, as we will see later.

Which of the two salts of a common ion will be precipitated depends on their relative solubility and the relative concentrations of the ions in question. If to a mixture of chloride and iodide ions is added a solution of silver ion,

silver iodide, yellow, is formed before silver chloride, white. This shows that AgI is less soluble than AgCl, or, in other words, I^- removes Ag^+ from solution more completely than does Cl^- at the same concentration. This would also enable us to predict that if we start with AgCl, we might bring about the following transformation quite readily:

$$AgCl + I^- = AgI + Cl^-,$$

whereas the reverse reaction could only be brought about by keeping the concentration of I^- very small and that of Cl^- very large, as would be the case in continual washing of the AgI precipitate on a filter with a solution of Cl^-. If, subsequently, we find that Ag_2CO_3, silver carbonate, is readily transposed into AgCl by allowing Cl^- to act upon it, then we know that Ag_2CO_3 is more soluble than either of the others, or, in other words, carbonate ion, CO_3^{--}, removes Ag^+ from solution less completely than either Cl^- or I^-, and without trying it, we could predict with assurance that the following reaction would take place very readily as read from left to right, but not in the reverse direction:

$$Ag_2CO_3 + 2\,I^- = 2\,AgI + CO_3^{--}.$$

Again, on finding by experiment that AgI is readily changed into Ag_2S by SH^-, we could conclude that both of the other precipitates could be transposed into Ag_2S still more easily. It will be seen that with the aid of the ideas of equilibrium we are able to predict a large number of reactions on the basis of a few well-chosen experiments, and thus utilize our experimental knowledge to the best advantage.

The same considerations apply to insoluble acids and bases. Magnesium hydroxide, $Mg(OH)_2$, when put into water, dissolves slightly, forming its ions as follows:

$$Mg(OH)_2 = Mg^{++} + 2\,OH^-.$$

Therefore if solutions of, say, magnesium chloride and sodium hydroxide are mixed, a precipitate of $Mg(OH)_2$ will be formed.

Since knowledge of the solubilities of salts, acids and bases in water is evidently extremely important in enabling one to predict and control reactions, some useful generalizations are given below.

As far as the relation between solubility and other properties is concerned, we may note that, other things being equal, **the higher the melting point of the compound the less soluble it will be**, not only in water, but in any solvent. Also, where the melting points are approximately the same, **the compounds most soluble in water will be those in which there is the greatest difference in the positive and negative character of the constituent parts** (see Chapter V), so that the salts of a metal like silver will be less soluble than those of a metal like potassium. These rough conclusions are illustrated by the values in the following table:

Substance	Melting Point	Solubility at 20°, in Mols per 1000 Grams of Solution
$CaCl_2 : 6\ H_2O$	30°	1.9
H_3BO_3	185°	0.077
$AgNO_3$	218°	4.3
$NaNO_3$	333°	5.5
$AgCl$	455°	0.00001
KCl	722°	3.3
$BaCO_3$	795°	0.0001
Ag_2S	830°	0.00001
$PbSO_4$	1100°	0.00015
CaF_2	1400°	0.0002
$CaSiO_3$	1510°	0 +
$BaSO_4$	1580°	0.00001

A number of statements may be made regarding the compounds of particular ions such as the following. It must be understood, however, that only the commoner compounds are considered:

All nitrates are soluble.

All acetates are soluble ($AgC_2H_3O_2$ only moderately).

All chlorides are soluble, except AgCl, HgCl, $PbCl_2$ (the last is sparingly soluble in cold water, moderately soluble in hot).

All sulfates are soluble, except $BaSO_4$, $PbSO_4$ ($CaSO_4$ and Ag_2SO_4 are sparingly soluble).

All carbonates and phosphates are insoluble, except those of sodium, potassium and ammonium. (Many acid phosphates are soluble, *e.g.*, $Mg(H_2PO_4)_2$, $Ca(H_2PO_4)_2$ and $Ba(H_2PO_4)_2$.)

All hydroxides are insoluble, except NaOH, KOH, NH_4OH and $Ba(OH)_2$; $Ca(OH)_2$ is sparingly soluble.

All sulfides are insoluble, except those of sodium, potassium and ammonium. Those of magnesium, calcium, barium and aluminum are not precipitated from solution because they are decomposed by water.

All salts of sodium, ammonium and potassium are soluble, except K_2PtCl_6, $(NH_4)_2PtCl_6$, $K_3Co(NO_2)_6$, $Na_4Sb_2O_7$.

All silver salts are insoluble, except $AgNO_3$, $AgC_2H_3O_2$, Ag_2SO_4 (the last two are moderately soluble).

It is upon the basis of solubilities that different ions present in the same solution may be separated. Suppose, for example, that a solution contained the nitrates of silver, barium, zinc and potassium. The addition of chloride ion, using, say, a solution of ammonium chloride, would precipitate the silver ion as AgCl, which could be filtered out.

The addition, then, of sulfate ion, as by using ammonium sulfate solution, would precipitate the barium ion as $BaSO_4$. After this is filtered out, the zinc ion could be precipitated as sulfide, using ammonium sulfide. The excess of ammonium salts in the solution could finally be removed by evaporating the solution to dryness and heating the residue, which would volatilize the ammonium salts, leaving only the potassium salts.

Ionization of Water. It was shown in Chapter X that water is an extremely weak electrolyte, dissociating to a minute extent as follows:

$$H_2O = H^+ + OH^-.$$

In pure water we have $(H^+) = (OH^-) = 10^{-7}$ mols per liter. This is very slight indeed, but we shall see that it is very important. If an excess of either of the ions H^+ or OH^- is added to water, as in dissolving an acid or base in it, the result is a diminution in the concentration of the other. If, for example, 0.001 *M* HCl is present, concentration of the hydrogen ion is increased 10,000 times, which will cause that of the hydroxide ion to decrease 10,000 times, becoming 10^{-11}.

The concentration of H^+ and OH^- in a solution may be estimated approximately by the aid of indicators (see p. 77). The following table gives the concentrations of H^+ and OH^- between normal H^+ and normal OH^-, together with the corresponding colors shown by several of the common indicators:

	Acid						"Neutral Point"			Alkaline				
Conc. of H^+	1	0.1	0.01	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
Conc. of OH^-	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	0.01	0.1	1
Methyl Violet	yellow	green	blue	violet →											
Methyl Orange				← red	orange	yellow →									
Litmus							← red	purple	blue →						
Phenolphthalein							← colorless		red →						color-less
Tri-nitrobenzene										← colorless			orange		

We may conclude, from the slightness of this ionization, that the reverse reaction will take place almost completely, so that whenever an acid and a base are mixed they will react almost completely to form water, leaving the other ions in solution, unless they happen to form an insoluble substance. We must therefore regard neutralization of acids and bases as taking place because of the fact that water is almost entirely undissociated. In connection with the neutralization of weak acids and bases we will return later to this topic.

Ionization of Weak Acids, Bases and Salts. The fact that many acids, bases and salts are but slightly ionized, as set forth in Chapter X, furnishes other reasons for expecting certain reactions to take place, for the principles of equilibrium tell us that in such cases the corresponding ions will unite, when brought together, to an extent depending on the ionization of the substance. For example, because we know that acetic acid is weak, that is, but slightly ionized, we know that when hydrochloric acid, which gives a high concentration of H^+, is mixed with sodium acetate, which gives a high concentration of $C_2H_3O_2^-$, these ions will combine till one or both are almost used up. Although sodium acetate is not a base, but a salt, we see that it has the effect of reducing high acidity. Similarly, because NH_4OH is a weak base it can be prepared from any ammonium salt by the action of any strong base, since NH_4^+ and OH^- unite rather completely. This property is used as a test for NH_4^+, and also in the manufacture of NH_3. Considerable ammonia is given off when coal is distilled, as in making gas and coke. This is extracted from the gas by washing in sulfuric acid, forming $(NH_4)_2SO_4$. When this salt is acted upon by slaked

lime, $Ca(OH)_2$, which gives a sufficiently high concentration of OH^-, there is set free NH_4OH, which breaks up at the temperature applied into NH_3 gas and H_2O. It is evident, in general, that weak acids should be liberated from their salts in solution by the action of stronger acids, and that weak bases should be liberated in like manner by strong bases.

An important application of this principle is in making "super-phosphate" for fertilizer. Tri-calcium phosphate (normal calcium phospate), $Ca_3(PO_4)_2$, occurs in bones and mineral deposits, but is so insoluble that even though finely ground it does not furnish plants at all freely with the phosphate necessary for their growth. Accordingly the more soluble di-calcium phosphate is produced by the action of concentrated sulfuric acid, as represented by the equation,

$$Ca_3(PO_4)_2 + H_2SO_4 = 2\ CaHPO_4 + CaSO_4.$$

Where the ions of several weak acids are competing for an insufficient amount of hydrogen ion, it is evident that the weakest acid will be formed first, the next weakest second, etc. In a mixture of $C_2H_3O_2^-$ and CO_3^{--}, the values on page 140, or page 168, make it evident that if H^+ is added to the solution gradually, the first reaction to take place will be

$$H^+ + CO_3^{--} = HCO_3^-,$$
$$\text{followed by } H^+ + HCO_3^- = H_2CO_3,$$
$$\text{followed by } H^+ + C_2H_3O_2^- = HC_2H_3O_2.$$

Complex Ions. As a rule the positive ions in solution are very simple, consisting nearly always only of a metallic atom, with its ionic charge or charges. There are, however, some cases where these simple ions can unite with other

ions or neutral molecules and still remain in solution as a more **complex ion**. They may best be considered in groups, according to the substances which are prone to form them.

(*a*) **Ammonia Complexes.** A solution of ammonia in water yields all of the substances denoted in the equation,

$$NH_3 + H_2O = NH_4OH = NH_4^+ + OH^-.$$

Ordinarily, when this solution is added to one containing an ion of a heavy metal, there is enough OH^- present to precipitate the metallic hydroxide. If, however, more of the ammonia solution is added, the concentration of NH_3 will increase faster than that of OH^-, and there results, in the case of certain metallic ions, notably Cu^{++}, Ni^{++}, Cd^{++}, Zn^{++}, Ag^+ and Cu^+, a solution which contains a complex positive ion containing both metal and ammonia. With the divalent cations the complex ions seem all to contain 4 NH_3, while those of the mono-valent ions contain 2 NH_3, so that the formulas are as follows: $Cu(NH_3)_4^{++}$, $Ni(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$, $Ag(NH_3)_2^+$, $Cu(NH_3)_2^+$. Since the NH_3 is a neutral molecule its presence does not alter the original ionic charge. In the cases of copper and nickel, these ammonia complexes are a deep blue in color, furnishing rather delicate tests for the presence of these metals. On account of this behavior the effect of an excess of ammonia is always to use up most of the free ions of these metals, with corresponding effects upon other equilibria, as will be explained later.

(*b*) **Cyanide Complexes.** Cyanide ion has the power to form complexes with a large number of metallic ions. In this case the metals are contained in the cation, as illustrated by the equation for the formation of the silver cyanide complex ion:

$$Ag^+ + 2\,CN^- = Ag(CN)_2^-.$$

(When Ag^+ is present in any considerable amount, AgCN is first precipitated, dissolving in excess of CN^-.)

Among these complexes may be mentioned the following:

$Cu(CN)_2^-$, $Zn(CN)_4^{--}$, $Au(CN)_2^-$, $Au(CN)_4^-$, $Pt(CN)_4^{--}$, $Pt(CN)_6^{--}$, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, $Ni(CN)_4^{--}$, $Co(CN)_6^{----}$, $Co(CN)_6^{---}$.

(*c*) **Complex Halides.** Many metallic ions, especially those of the noble metals, have a tendency to form complex halides. This is particularly strong in the case of gold, platinum and the other "platinum metals," as shown in the following: $AuCl_2^-$, $AuCl_4^-$, $PtCl_6^{--}$.

(*d*) **Complex Oxalates.** Certain metallic ions form complex oxalates with oxalate ion, $C_2O_4^{--}$, as exemplified by $Fe(C_2O_4)_3^{---}$.

Competition between the Foregoing Factors. We have seen, in a few instances, how reactions are determined by competition between the various ions of weak acids, or the relative solubilities of various salts of the same ion. We are now prepared to discuss competition between the different factors, volatility, solubility, ionization of water, weak acids, bases and salts, complex ions, and to consider general examples of the control of reactions.

(*a*) **Hydrolysis.** When the salt of a weak acid is dissolved in water we have present in the solution an ion that has a great tendency to combine with hydrogen ion. Now water, though it is such a weak electrolyte, yields some hydrogen ion. Consequently, there is a slight formation of the weak acid, with a resulting decrease in the concentration of the hydrogen ion and a corresponding increase in the concentration of the hydroxide ion. To say this

concretely, let us consider a solution of sodium acetate, which gives a large concentration of Na^+ and $C_2H_3O_2^-$. Now, since the water yields a trace of H^+ and OH^-, and since $HC_2H_3O_2$ is a weak acid, there will be some union of H^+ and $C_2H_3O_2^-$ to form the acid, liberating an excess of OH^-, so that the solution will be slightly alkaline. This may be expressed by an equation as follows:

$$C_2H_3O_2^- + H_2O = HC_2H_3O_2 + OH^-.$$

It will be observed that this reaction is the reverse of the neutralization of acetic acid with a strong base, and since the latter reaction is nearly complete, of course the former can take place but slightly under similar conditions. In writing the equation we show the net effect of what has happened, as expressed previously in words. We must guard against the error of thinking that the formulas on the right-hand side of the equation tell what is in the solution after equilibrium is reached. The solution still contains mostly $C_2H_3O_2^-$ and H_2O, which fact is expressed by saying that the above substances react only slightly before equilibrium is reached, not by writing their formulas on both sides of the equation. Moreover, in a single equation like this, we should not write water as ionized, for the bulk of it is un-ionized. As a matter of fact, there are two simultaneous reactions occurring, as follows:

$$C_2H_3O_2^- + H^+ = HC_2H_3O_2, \text{ and } H_2O = H^+ + OH^-.$$

The sum of these two gives the former.

Obviously there is a competition between $C_2H_3O_2^-$ and OH^- for the H^+, as might be represented in this way:

$$\begin{array}{l} HC_2H_3O_2 = C_2H_3O_2^- + H^+ \\ \qquad\qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad\qquad\quad OH^- \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad H_2O. \end{array}$$

That the OH^- should get or keep most of the H^+ is to be expected from the fact that water is vastly less ionized than is acetic acid. It is this disparity between the ionization of the two substances that enables $C_2H_3O_2^-$ to set free but a slight amount of OH^- from water, on the one hand, and which causes neutralization of $HC_2H_3O_2$ by OH^- to be nearly complete, on the other hand.

If, instead of an acetate, we dissolve in the water the salt of some weaker acid, like sodium phenolate, $NaOC_6H_5$ (the " phenol sodique " of the drug store), we have in phenolate ion, $OC_6H_5^-$, one which will unite with the hydrogen ion of water more completely than will acetate ion, forming HOC_6H_5, the acid known as phenol, or carbolic acid, and setting free from the water more OH^- than in the case of sodium acetate. The competition for H^+ is here between OH^- and $OC_6H_5^-$, and though the latter gets but little of it, since carbolic acid is much more ionized than water, it nevertheless gets more than does acetate ion. We may express this competition in the same manner as before,

$$\begin{array}{l} HOC_6H_5 = OC_6H_5^- + H^+ \\ \qquad\qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad\qquad\quad OH^- \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad H_2O. \end{array}$$

The net result we may write, as before,

$$OC_6H_5^- + H_2O = HOC_6H_5 + OH^-.$$

The discussion shows why "phenol sodique" can be used as a mild antiseptic. Its solution always contains free carbolic acid, which is an antiseptic, and though its concentration is small, if it is used up more can be formed from the above equilibrium to replace it.

A process such as this is called "hydrolysis." The idea underlying the name is that a salt is split up by water into free acid and base. We see that salts of weak acids always hydrolize in aqueous solution on account of the possibility of forming the free weak acid. Of course, the ions giving weak bases also take part in hydrolysis. All ammonium salts are hydrolyzed, because of the formation of the weak base, ammonium hydroxide, as illustrated by the equation,

$$NH_4^+ + H_2O = NH_4OH + H^+,$$

where the solution becomes slightly acid. If the salt is one of both a weak acid and a weak base, like ammonium acetate, $NH_4C_2H_3O_2$, both of its ions take part in hydrolysis, as shown by the equation,

$$NH_4^+ + C_2H_3O_2^- + H_2O = NH_4OH + HC_2H_3O_2.$$

In a case like this the acidity or alkalinity of the resulting solution depends upon whether the acid or the base is weaker. In this case they are of almost identical strength, as may be seen from the values on page 140, so that the solution is almost neutral, though it does contain more NH_4OH than a solution of NH_4Cl, and more free $HC_2H_3O_2$ than one of $NaC_2H_3O_2$, since both of the ions present aid in splitting up the water.

Hydrolysis plays an important part in many reactions, a few examples of which will be given. It is desirable that solutions to be used for household cleaning should have a slightly alkaline reaction, since this aids in emulsifying grease and removing dirt, and also tends to soften hard water, as will be explained later. It is not desirable, however, to use a strong base like sodium hydroxide, because this gives too great a concentration of OH^-, which has injurious effects on the hands and on some fabrics, unless used in very dilute solution, where the slight amount of OH^- would soon be used up. What is wanted is a solution containing but little free OH^-, but which is able to yield more should this be used up. Such is the case with ammonia, so that it finds large use in the home. We see also that salts of weak acids fulfill these conditions, and several of them find extensive application as cleansing agents. Sodium carbonate, Na_2CO_3, is the salt of a very weak acid, and its solutions give a very marked alkaline reaction, as follows:

$$CO_3^{--} + H_2O = HCO_3^- + OH^-.$$

On this account it is extensively known and used as "washing soda." There are two sodium carbonates, this one and $NaHCO_3$, sodium acid carbonate. The solution of the latter also undergoes hydrolysis,

$$HCO_3^- + H_2O = H_2CO_3 + OH^-.$$

However, since H_2CO_3 is considerably more dissociated than HCO_3^-, according to the figures given on page 140, the former will be formed from HCO_3^- and H^+ less completely than the latter will be from CO_3^{--} and H^+. Hence the solution of Na_2CO_3 is much more alkaline than one of $NaHCO_3$, and is used as "washing soda," whereas the latter

is used only where a much less alkaline reaction is desired, as for internal use. The $NaHCO_3$, on the other hand, is "baking soda," because it can yield much more CO_2 for the same weight both of itself and acid.

Borax, sodium borate, is the salt of the very weak boric acid, and has the same effect in cleansing as sodium carbonate. Sodium silicate, the salt of weak silicic acid, behaves in the same way, and is a constituent of laundry soaps.

Aluminum hydroxide, $Al(OH)_3$, is not only insoluble, but is a weak base as well, so that aluminum ion, Al^{+++}, in water forms some of the hydroxide, liberating the hydrogen ion and causing the solution to become distinctly acid. On this account aluminum salts can be used to liberate carbon dioxide from carbonates, as is done in the alum baking powders. A similar reaction is used by oil companies in a scheme for extinguishing gasoline or petroleum fires on oil tanks. The sodium carbonate solution and one of aluminum sulfate, containing glue to produce a froth, which retains the CO_2 gas, are projected from adjacent pipes over the burning tank, when the froth produced spreads over the fire and quenches it.

Due to hydrolysis of aluminum ion with ions of very weak acids aluminum salts of these cannot exist in the presence of water. When CO_3^{--} is added to Al^{+++}, $Al(OH)_3$ is precipitated instead of a carbonate; and aluminum sulfide, prepared directly from the elements, when put into water, decomposes completely as follows:

$$Al_2S_3 + 6\,H_2O = 2\,Al(OH)_3 + 3\,H_2S.$$

There are a number of other compounds, such as the chlorides of the non-metals, that undergo complete hy-

drolysis. When PCl_3, phosphorus tri-chloride, is put into water the following reaction takes place:

$$PCl_3 + 3\,H_2O = P(OH)_3 + 3\,H^+ + 3\,Cl^-.$$

The hydroxide of phosphorus is so completely an acid rather than a base that the above reaction is complete.

Bismuth chloride undergoes hydrolysis readily. In a case like this the hydrolysis doubtless takes place in steps, and we have successively, Bi^{+++}, $Bi(OH)^{++}$, $Bi(OH)_2^+$, or its anhydride, BiO^+, and finally $Bi(OH)_3$, or its anhydride. When bismuth chloride solution is used the chloride ion is capable of forming an insoluble precipitate with the bismuthyl ion, BiO^+, so that the hydrolysis takes place as follows:

$$Bi^{+++} + Cl^- + H_2O = BiOCl + 2\,H^+.$$

The addition of sufficient H^+ of course reverses the reaction and dissolves the precipitate. Similar reactions are obtained with bismuth nitrate and with antimonous and antimonic chlorides.

In titrating a weak acid with a strong base, or vice versa, it is necessary to determine, not when the solution is neutral, but when it contains equivalent amounts of acid and base, a minute proportion of which will be free, giving an alkaline or acid reaction, as the case may be. If sodium acetate, for example, is dissolved in water, the solution is slightly alkaline, although equivalent amounts of acid and base are present. To reproduce this condition, when acetic acid is titrated with sodium hydroxide, one should use an indicator like phenolphthalein, which, as shown on page 181, changes color in a solution which is faintly alkaline, so that a slight excess of either acid or base would affect the indicator.

Similarly, in titrating ammonia with hydrochloric acid, we wish to end with the solution not really neutral but slightly acid, since a solution of ammonium chloride reacts slightly acid. Hence an indicator like methyl orange, according to the table on page 181, would be suitable for this purpose. In general, the proper indicator to use in a titration may be found by taking the normal salt which will result from the titration, dissolving it in water, and determining what indicator will change color when a drop of solution of the free acid or base is added in excess.

(*b*) **The Solution of Hydroxides.** We have seen that when a more or less insoluble metallic hydroxide is in contact with water it gives to the water a certain amount of its ions, equilibrium being reached the sooner the less soluble the hydroxide. As an example we may consider magnesium hydroxide, $Mg(OH)_2$, which gives a small concentration of ions as follows:

$$Mg(OH)_2 = Mg^{++} + 2\,OH^-.$$

We have seen also that hydrogen ion has a very great tendency to unite with hydroxide ion. If, therefore, H^+ is added to the precipitate of magnesium hydroxide suspended in water, there will be a competition between the H^+ and the Mg^{++} for the OH^-, which may be represented, as before, by the double equation,

$$\begin{array}{r} Mg(OH)_2 = Mg^{++} + 2\,OH^- \\ + \\ 2\,H^+ \\ \| \\ 2\,H_2O. \end{array}$$

Now, since water is so extremely undissociated we might expect that the H^+ added would be successful in stealing

the OH^- away from the magnesium ion, liberating the latter, which would thus go into solution so that the effect of the acid would be to dissolve the precipitate. The total reaction is therefore

$$Mg(OH)_2 + 2\,H^+ = Mg^{++} + 2\,H_2O.$$

As a matter of fact, water is formed so completely from its ions that it takes but a moderate concentration of acid to dissolve practically all hydroxides.

Our principles of equilibrium would lead us to expect that any substance that would unite with OH^- would have the effect of dissolving insoluble bases. Besides H^+, we have found that NH_4^+ is a substance which has a tendency to unite with OH^- to form the weak base NH_4OH. We know, however, that these two ions do not unite nearly so completely as do H^+ and OH^-, therefore we should not expect NH_4^+ to be nearly as effective as H^+ in dissolving bases. It is true that the solubility of any base will be increased by the presence of NH_4^+, but if the base is very insoluble to begin with, the increase may not be sufficient to bring the amount in solution up to a value such that we would call it soluble. Suppose, for example, that the solubilities of two bases in water are 0.001 and 0.000001 molal respectively, and that the addition of a certain amount of NH_4^+ is enough to increase each 1000 times. The effect would be to make the solubilities of the two bases now 1 molal and 0.001 molal, respectively. We would then call the first soluble in NH_4^+, but the second, insoluble. Among the insoluble bases which may be thus dissolved in NH_4^+ are $Mg(OH)_2$, $Ca(OH)_2$, $Zn(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$.

o

(*c*) **The Solution of Oxides.** Oxides of metals are much like the corresponding hydroxides, and may either be converted into hydroxides, in some cases, or produced from them by heating. The solubility of hydroxides in H^+ leads us to expect that oxides will likewise dissolve in acids. We may think here of the formation of water from the H^+ of the acid and the oxygen of the oxide. Most oxides, indeed, are easily dissolved in acids, though more difficultly than are the corresponding hydroxides. This difficulty may be largely a matter of the speed of the reaction. In a few instances, notably Fe_2O_3, Cr_2O_3, and Al_2O_3, if they have been heated to a very high temperature they become practically insoluble in acids.

(*d*) **Amphoteric Hydroxides.** There are several metallic hydroxides that are capable of acting either as weak bases or weak acids. Any substances that behave in this way are called **amphoteric**. Such a substance may give to water not only the metallic cation and the OH^- of a base, but also H^+ and a corresponding anion. Taking $Al(OH)_3$ as an example, we may express this double power of dissociating as follows:

$$Al^{+++} + 3\ OH^- = Al(OH)_3 = H^+ + H_2AlO_3^-.$$

As is the case with most weak polybasic acids, the various hydrogen ions dissociate in steps, and since H_3AlO_3 is an exceedingly weak acid, even the first H^+ is ionized with difficulty, and the second and third are practically unionized unless a large excess of OH^- is added. From the double equilibrium that we have represented it will be seen that the precipitate can be dissolved not only by the addition of H^+, which would act as follows:

$$Al(OH)_3 + 3\ H^+ = Al^{+++} + 3\ H_2O,$$

but also by the addition of OH^-, which would act in the following way,

$$H_3AlO_3 + OH^- = H_2O + H_2AlO_3^-.$$

It is possible, therefore, to have aluminum present either in an alkaline or in an acid solution, while in a solution approximately neutral it cannot exist, but will be precipitated as $Al(OH)_3$.

Other hydroxides behaving in this way are those of zinc, chromium, lead and tin (both stannous and stannic). This amphoteric character may be made use of in separating from each other metallic ions existing in the same solution. Thus Fe^{+++} is commonly separated from Al^{+++} and Cr^{+++} by adding concentrated OH^- in excess, which leaves the first precipitated as $Fe(OH)_3$, but dissolves the others as aluminate and chromite ions respectively.

(*e*) **The Solution of Sulfides in Hydrogen Ion.** The similarity between oxides and sulfides has been previously pointed out, page 69, also the fact that hydrogen sulfide is a very weak electrolyte, like water. It is but a slight transition, therefore, from the consideration of oxides to that of sulfides. The chief difference to be noted is that whereas reactions like the following are very numerous,

$$Zn^{++} + 2\,OH^- = Zn(OH)_2,$$

the corresponding reaction, when sulfur is substituted for oxygen, is the formation of a sulfide, rather than a hydrosulfide, as shown by the reaction

$$Zn^{++} + 2\,SH^- = ZnS + H_2S.$$

This is analogous to what takes place with OH^- in the case of Ag^+, and, when the solution is boiled, with Cu^{++}, as shown by

$$2\,Ag^+ + 2\,OH^- = Ag_2O + H_2O,$$

and $$Cu^{++} + 2\,OH^- = CuO + H_2O.$$

The solution of a sulfide in an acid depends upon the removal of the sulfide ion by the hydrogen ion of the acid to form hydrogen sulfide, H_2S, and its precipitation depends upon the presence of sufficient sulfide ion. This competition between the metallic ion and the hydrogen ion for the sulfide ion may be represented by the scheme used before,

$$\begin{array}{l} ZnS = Zn^{++} + S^{--} \\ \qquad\qquad\quad + \\ \qquad\qquad 2\,H^+ \\ \qquad\qquad\quad \| \\ \qquad\qquad H_2S. \end{array}$$

Some sulfides are so insoluble that the metallic ion finds enough sulfide ion to be precipitated even when the solution contains a moderately concentrated acid. These sulfides, conversely, will not be dissolved by hydrogen ion in moderate concentrations. The sulfides which behave in this way include Ag_2S, HgS, PbS, Bi_2S_3, CuS, As_2S_3, As_2S_5. Next, we have several, including CdS, Sb_2S_3, Sb_2S_5, SnS, SnS_2, that will dissolve if the H^+ is concentrated but not if it is dilute. Then follow ZnS, MnS, FeS, NiS, CoS, which are so soluble that dilute H^+ is sufficient to prevent their precipitation. The cases of NiS and CoS are peculiar in that they are not precipitated in acid solution, but nevertheless will not dissolve at all rapidly in dilute acid if first precipitated from an alkaline solution. This may be due to the existence of two modifications of the solids, so that when the more soluble modification is once precipitated it changes over into the insoluble modification; or it may be an example of slow rate of reaction, similar to the slow reac-

tion between certain acids and oxides, as referred to on page 194. In order to precipitate this group of sulfides it is necessary to have a neutral or slightly alkaline solution so that sufficient sulfide ion can be present. The usual reagent is a solution of ammonium sulfide, made by passing H_2S into NH_4OH solution. If acetic acid is used, it is possible, by adding acetate ion, to reduce the concentration of H^+ sufficiently to allow the precipitation of ZnS.

In dissolving a sulfide in H^+, as represented by the equation

$$Sb_2S_3 + 6\ H^+ = 2\ Sb^{+++} + 3\ H_2S,$$

we have been considering the effect of the concentration of H^+, and have seen that the less soluble the sulfide the more concentrated must be the H^+ in order to dissolve it. Another factor may be introduced by virtue of the volatility of H_2S. If the solution is boiled, the H_2S is more readily removed, so that more can form, resulting in an easier and more rapid solution of the sulfide. To dissolve the less soluble sulfides the use of concentrated H^+, together with boiling the solution, is insufficient, and we shall see in Chapter XV that it is necessary to destroy the H_2S by an oxidizing agent.

The order of solubility of the above sulfides in water is roughly as follows, beginning with the most soluble: MnS, FeS, ZnS, NiS, CoS, SnS_2, SnS, Sb_2S_3, CdS, PbS, Bi_2S_3, CuS, As_2S_5, Ag_2S, HgS.

(*f*) **Amphoteric Sulfides.** We have seen above how several hydroxides can dissociate in two ways, so as to be able to dissolve either in H^+ or in OH^-. There are, likewise, three sulfides which can dissolve in both OH^- and SH^-, namely, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2. These same elements, it will be recalled, give oxides and hydroxides which dissolve in alkalies.

The analogy between the oxides and sulfides may be brought out in the following parallel reactions:

$$As_2O_5 + 6\,OH^- = 2\,AsO_4^{---} + 3\,H_2O;$$
$$As_2S_5 + 6\,SH^- = 2\,AsS_4^{---} + 3\,H_2S;$$
$$As_2O_5 + 2\,OH^- = 2\,AsO_3^- + H_2O;$$
$$As_2S_5 + 2\,SH^- = 2\,AsS_3^- + H_2S.$$

Since there is undoubtedly more S^{--} in an alkaline sulfide solution than there is O^{--} in the presence of OH^-, we sometimes prefer to express the reaction for the solution of these sulfides by equations such as the following, which are a little simpler than the above, though they do not bring out the analogy with the corresponding oxygen compounds quite as well:

$$As_2S_5 + 3\,S^{--} = 2\,AsS_4^{---} \text{ or } As_2S_5 + S^{--} = 2\,AsS_3^-;$$
$$As_2S_3 + 3\,S^{--} = 2\,AsS_3^{---} \text{ or } As_2S_3 + S^{--} = 2\,AsS_2^-;$$
$$SnS_2 + S^{--} = SnS_3^{--}.$$

The compounds in which the metals have the lower valence are always less acidic, both in the case of the oxides and the sulfides, and Sb_2S_3 dissolves with some difficulty in ammonium sulfide, and SnS is practically insoluble in the same. In dissolving both of these sulfides yellow ammonium sulfide is used, which contains polysulfide ions, like S_2^{--}. This is capable of dissolving the lower sulfides of all three metals, changing them to the sulfo-ion of the higher valence, thus,

$$Sb_2S_3 + 2\,S_2^{--} + S^{--} = 2\,SbS_4^{---},$$

or

$$Sb_2S_3 + S_3^{--} = 2\,SbS_3^-,$$
$$SnS + S_2^{--} = SnS_3^{--}.$$

When acid is added to the solutions of the above sulfo-ions the weak acid, H_2S, is produced, reprecipitating the

sulfides, just as the addition of acid to stannate ion reprecipitates the stannic hydroxide. This reprecipitation consists simply in the reversal of the reactions whereby these sulfo-ions are produced.

The different behaviors of sulfides towards the H^+ and SH^- or S^{--} is made the basis of important separations in both qualitative and quantitative analysis. If a solution contained the following ions, Pb^{++}, Bi^{+++}, Cu^{++}, As^{+++}, Sb^{+++}, Sn^{++}, Zn^{++}, Mn^{++}, Mg^{++}, they could be divided into groups by controlling the concentrations of the substances in the equilibrium.

$$H_2S = H^+ + SH^- = 2\,H^+ + S^{--}.$$

This separation can best be outlined by the aid of a diagram.

<table>
<tr><td colspan="4">Have dilute H^+ (HCl) present, and pass in H_2S</td></tr>
<tr><td colspan="3">Precipitate insoluble
PbS, Bi_2S_3, CuS, As_2S_3, Sb_2S_3, SnS
Treat with S_2^{--}
(yellow ammonium sulfide)</td><td>In solution
Zn^{++}, Mn^{++}, Mg^{++}
Make alkaline, add
$S^{--}(SH^-)$
(ammonium sulfide)</td></tr>
<tr><td>Left insoluble,
PbS, Bi_2S_3, CuS</td><td colspan="2">In solution
AsS_3^-, SbS_3^-, SnS_3^{--}
Reprecipitate the sulfides
and heat with 12 NHCl</td><td>Precipitate
ZnS, MnS</td><td>In solution
Mg^{++}</td></tr>
<tr><td></td><td>Left
insoluble,
As_2S_5</td><td>In solution
Sn^{++++}, Sb^{+++},
dilute to 2 $N$$H^+$,
pass in H_2S cold,
ppt. Sb_2S_3</td><td></td><td></td></tr>
</table>

(*g*) **Salts of Other Weak Acids.** Salts of all weak acids are made more soluble by the addition of H^+. This increase in solubility, in the case of carbonates, is enough to bring all insoluble carbonates into solution in dilute H^+. A very interesting case of the solution of a carbonate was

alluded to on page 156. It is the reaction whereby hard water is produced from limestone rock. If very dilute H^+, as is present in very dilute HCl, is allowed to act upon $CaCO_3$, the CO_3^{--} which the latter gives to the solution in very slight amount is converted into HCO_3^- only, and not into H_2CO_3, as would be the case if more concentrated acid were used. The equation for this reaction is as follows:

$$CaCO_3 + H^+ + Cl^- = Ca^{++} + HCO_3^- + Cl^-.$$

If H_2CO_3 is used instead of HCl, it also can furnish sufficient H^+ to bring about essentially the same reaction,

$$CaCO_3 + H_2CO_3 = Ca^{++} + 2\,HCO_3^-.$$

Since most surface water contains some dissolved carbon dioxide, the above reaction takes place whenever such water flows over limestone. A quite analogous reaction occurs with $MgCO_3$. The reaction can be reversed by removing the H_2CO_3, either by boiling the solution, as occurs in a tea-kettle, whence the name "temporary hardness," or else by neutralizing it with some alkali, or some substance giving OH^- by hydrolysis, like sodium carbonate or borax. When this is done on a large scale, the water is analyzed and just the right amount of $Ca(OH)_2$ is added. Although more Ca^{++} is added in this way, there is produced enough CO_3^{--} to precipitate all of it; the total reaction is represented by the equation

$$2\,Ca^{++} + 2\,HCO_3^- + 2\,OH^- = 2\,CaCO_3 + 2\,H_2O.$$

When the hardness in water is produced by dissolving a salt like $CaSO_4$, it is necessary to add CO_3^{--} (as Na_2CO_3) to precipitate the Ca^{++}.

When the solubility of the hydroxide of a metal is about as small as the solubility of its carbonate, the latter will hydrolyze partly to give a basic carbonate. This is the case with the carbonates of copper, lead and mercury, as illustrated by $Pb(OH)_2 \cdot 2\,PbCO_3$, the "white lead" of the painter.

There are no phosphates so insoluble in water but that they are dissolved by moderately concentrated H^+. Although PO_4^{---} is the ion of the very weak acid, HPO_4^{--}, nevertheless dilute H^+ is not sufficient to dissolve all of the normal phosphates, both because some are so insoluble to begin with that the increase is not sufficient to make them soluble in the usual sense, and also because some monohydrogen phosphates, like $CaHPO_4$, are rather insoluble, and even though $Ca_3(PO_4)_2$ be converted into the former, solution does not result.

As a rule the acid salts are more soluble than the normal salts, as exemplified by the series of calcium phosphates. $Ca(H_2PO_4)_2$ is soluble, $CaHPO_4$ is insoluble and $Ca_3(PO_4)_2$ is very insoluble in water. The chief exception to this rule is furnished by the sodium carbonates, where the acid salt is the least soluble.

The industrial preparation of sodium carbonate by the Solvay process furnishes an interesting application of the principles here discussed. The normal salt, Na_2CO_3, is very soluble, but the acid salt, $NaHCO_3$, is not very soluble in the cold. The latter can therefore be precipitated by bringing together the ions Na^+ and HCO_3^- in sufficient concentration. To do this, NH_3 gas and CO_2 gas are led into a cold concentrated solution of NaCl. The acid and base produced by the solution of the gases in water react to give

NH_4^+ and HCO_3^-, provided they are used in the right proportion, and when the concentration of HCO_3^- reaches a sufficient value it begins to precipitate the Na^+ as $NaHCO_3$.*

(*h*) **Solution by Forming Weak Salts.** In the previous cases we have treated compounds which could be brought into solution by adding some substance, especially H^+, which would use up the anion of the precipitate. It is equally possible to dissolve a compound by adding some reagent that will use up the free cation. Thus lead sulfate, $PbSO_4$, may be dissolved by the addition of an acetate, because lead acetate is a soluble weak salt, and the acetate ion, if in sufficient concentration, can compete successfully with the sulfate ion for the lead ion, as shown by the equation,

$$PbSO_4\ (\text{solid}) + 2\ C_2H_3O_2^- = Pb(C_2H_3O_2)_2 + SO_4^{--}.$$

Similar effects are shown, at least to some extent, wherever weak salts, such as are mentioned on page 139, can be formed. We find, for example, that CdI_2 is a moderately weak salt, consequently the following reaction can be made to proceed to some extent by using a sufficient concentration of I^-:

$$CdS + 2\ I^- = CdI_2 + S^{--}.$$

(*i*) **Solution by Forming Complex Ions.** Wherever the cation is capable of forming a complex ion, a precipitate can be rendered more soluble than it is in water. Thus, a salt like $ZnCO_3$ can be dissolved, not only by using up the anion, as in adding H^+, but also by using up the cation, as when $Zn(NH_3)_4^{++}$ is formed by the addition of ammonia solution.

* This solid is separated from the solution and heated to produce Na_2CO_3 (cf. p. 208). The CO_2 given off during the heating is returned to the process. A fresh supply is obtained by heating $CaCO_3$, the CaO resulting is slaked to give $Ca(OH)_2$, which is used to recover the NH_3 from the NH_4^+.

The competition between the CO_3^{--} and the NH_3 may be represented as before:

$$\begin{array}{c} ZnCO_3 = Zn^{++} + CO_3^{--} \\ + \\ 4\ NH_3 \\ \| \\ Zn(NH_3)_4^{++}. \end{array}$$

If the concentration of the ammonia is sufficient, the complex ion is formed at the expense of the insoluble carbonate, resulting in the net reaction,

$$ZnCO_3 + 4\ NH_3 = Zn(NH_3)_4^{++} + CO_3^{--}.$$

In the case of ZnS, which is much less soluble, the formation of the complex ion cannot take place to an appreciable extent, so that ZnS is not dissolved by ammonia. The copper ammonia complex ion seems to be formed more completely than the corresponding zinc ion, so that traces of $Cu(NH_3)_4^{++}$ can be formed from CuS if concentrated ammonia is used, in spite of the smaller solubility of CuS.

(*j*) **Solution by Forming Ions of Amphoteric Hydroxides.** The effect of a considerable concentration of OH^- may be to dissolve the relatively insoluble salts of certain metals, in a fashion similar to that whereby complex ions are formed. In fact, these ions may be considered as complex ions. Most of the lead salts, for example, are dissolved by OH^-, as exemplified by the reaction,

$$PbSO_4 + 2\ OH^- = H_2O + HPbO_2^- + SO_4^{--}.$$

Even ZnS is not so insoluble but that it can be dissolved by concentrated OH^-.

(*k*) **Systematizing the Reactions of a Given Ion.** It is not necessary to perform and remember all of the reactions of a certain ion with a set of reagents in order to tell what they will be. It suffices to make an intelligent selection of a few of the possible reactions and arrange the resulting information systematically. As an example of what is meant let us consider a number of the reactions of silver ion, Ag^+, with the following: CO_3^{--}, OH^-, CN^-, Cl^-, Br^-, I^-, S^{--}, NH_3, $S_2O_3^{--}$. Let us assume that we have performed experiments which show that the reactions take place which are represented by the following equations as read from left to right:

$$AgCl + Br^- = AgBr + Cl^-,$$
$$AgCl + 2\,NH_3 = Ag(NH_3)_2^+ + Cl^-,$$
$$Ag(NH_3)_2^+ + I^- = AgI + 2\,NH_3,$$
$$Ag_2O + H_2O + 2\,Cl^- = 2\,AgCl + 2\,OH^-,$$
$$AgI + 2\,CN^- = Ag(CN)_2^- + I^-,$$
$$Ag_2O + H_2O + CO_3^{--} = Ag_2CO_3 + 2\,OH^- \text{ (easily reversed)},$$
$$AgBr + 2\,S_2O_3^{--} = Ag(S_2O_3)_2^{---} + Br^-,$$
$$Ag(S_2O_3)_2^{---} + I^- = AgI + 2\,S_2O_3^{--},$$
$$AgCl + CN^- = AgCN + Cl^-,$$
$$AgBr + 2\,NH_3 = Ag(NH_3)_2^+ + Br^- \text{ (easily reversed)},$$
$$2\,Ag(CN)_2^- + S^{--} = Ag_2S + HCN^-,$$
$$Ag_2CO_3 + 2\,Cl^- = 2\,AgCl + CO_3^{--},$$
$$AgCN + 2\,NH_3 = Ag(NH_3)_2^+ + CN^-.$$

From these observations it is possible to arrange the following list of substances in the order showing the completeness with which they unite with Ag^+ to form a precipitate or a complex ion as the case may be. It must be understood that the reagents forming complexes are taken in moderate excess:

Substance	To Form
OH^-	Ag_2O
CO_3^{--}	Ag_2CO_3
Cl^-	$AgCl$
CN^-	$AgCN$
NH_3	$Ag(NH_3)_2^+$
Br^-	$AgBr$
$S_2O_3^{--}$	$Ag(S_2O_3)_2^{---}$
I^-	AgI
CN^-	$Ag(CN)_2^-$
S^{--}	Ag_2S

In order to make this list it is necessary to make a minimum of eight observations, and from it it is possible to predict the direction of forty-five reactions. The list was made in such a way that each substance in the first column will steal Ag^+ away from its combinations with any substance above it, because less Ag^+ can exist in the same solution with substances farther down the column than with those higher up at the same concentration. Thus AgBr gives to the solution more Ag^+ than can exist together with I^-, hence the following reaction will readily take place:

$$AgBr + I^- = AgI + Br^-.$$

For the same reason, AgI will dissolve in CN^-, and also any precipitate in the above list can be transposed into AgI by I^- except Ag_2S. Where two substances have about the same power to combine with Ag^+, as is the case with NH_3 and Br^-, it is possible to reverse the reaction by altering the concentrations. Thus the reaction,

$$AgBr + 2\,NH_3 = Ag(NH_3)_2^+ + Br^-,$$

can be made to take place as read from left to right or from right to left, according as the concentration of NH_3 or that of Br^-, respectively, is taken in sufficient excess.

By adding to the information given by the above list a few facts about the other reactions of the substances, we are able to predict a very large number of reactions. For example, HCN is a very weak acid, hence AgCN can be dissolved by H^+. For the same reason, H^+ will liberate Ag^+ from a solution of $Ag(CN)_2^-$, and if Cl^- is present along with the H^+, then AgCl will be precipitated as follows:

$$Ag(CN)_2^- + 2\,H^+ + Cl^- = AgCl + 2\,HCN.$$

In similar fashion, AgCl will be dissolved by NH_3, according to the reaction represented earlier, but will be reprecipitated on the addition of H^+, which takes up the NH_3 to form NH_4^+, allowing the Ag^+ to recombine with the Cl^- left from the previous reaction, as shown by the equation:

$$Ag(NH_3)_2^+ + 2\,H^+ + Cl^- = AgCl + 2\,NH_4^+$$

Again, since Ag_2SO_4 is moderately soluble (see page 179) we see that it can be readily transposed to AgCl by dissolving it in water and adding Cl^-, as AgCl is insoluble. In order to reverse this transposition we see that some other principle besides solubility must be invoked. If water is absent, we can take advantage of the greater volatility of HCl as compared with H_2SO_4, so that the reaction,

$$2\,AgCl + H_2SO_4 = Ag\,SO_4 + 2\,HCl,$$

can be brought about by heating AgCl with concentrated H_2SO_4.

Miscellaneous Transformations. The general application of the above principles and information can be illustrated by further miscellaneous examples.

To change $CaSO_4$ to $CaCO_3$ we can take advantage of the greater solubility of the former (see page 179) and treat it with a solution of a soluble carbonate, like Na_2CO_3, which gives CO_3^{--}, when the insoluble $CaCO_3$ would be precipitated. The manner of expressing this in an equation would depend upon whether the amount of water present is such that the $CaSO_4$ is mainly present as solid or as dissolved ions. These cases would be represented respectively as follows:

$$CaSO_4 + CO_3^{--} = CaCO_3 + SO_4^{--},$$
$$Ca^{++} + SO_4^{--} + CO_3^{--} = CaCO_3 + SO_4^{--}.$$

To bring about the reverse transformation we would have to make up for the greater solubility of $CaSO_4$, which shifts the equilibrium towards $CaCO_3$, by adding H^+, which would use up CO_3^{--} and reverse the reaction.

To change $ZnSO_4$ to $ZnCl_2$ it is necessary to replace SO_4^{--} by Cl^-. This might be done by adding $BaCl_2$ to a solution of the $ZnSO_4$, giving the reaction,

$$Zn^{++} + SO_4^{--} + Ba^{++} + 2\,Cl^- = BaSO_4 + Zn^{++} + 2\,Cl^-.$$

If exactly the right amount of $BaCl_2$ were used, all of the Ba^{++} and SO_4^{--} present would precipitate each other, leaving in solution Zn^{++} and Cl^-, and if the precipitate were filtered out and the solution evaporated, these ions would combine to give solid $ZnCl_2$, as desired. However, it is difficult to add just the equivalent amount of $BaCl_2$, and it is accordingly better to use a different method, with reagents an excess of which can be easily removed. Since $Zn(OH)_2$ is insoluble, it can be precipitated by adding OH^- (*e.g.*, NaOH solution) to the solution of $ZnSO_4$. If the precipitate is now filtered out, the SO_4^{--} is disposed of. The precipitate of $Zn(OH)_2$ can now be dissolved by HCl solu-

tion, since the H^+ of the acid unites so strongly with the OH^- of the base, giving a solution containing Zn^{++}, with H^+ and Cl^- in excess. If, now, this solution is evaporated, the excess of H^+ and Cl^- go off along with the water, as HCl gas, leaving finally solid $ZnCl_2$. By precipitating the carbonate, $ZnCO_3$, instead of the hydroxide, the same transformation can be made, since $ZnCO_3$ is equally soluble in the stronger acids. In fact, a soluble salt of any metal which has an insoluble hydroxide or carbonate can be transposed to another soluble salt of the same metal by precipitation of one of these and dissolving it in the acid corresponding to the desired salt.

Aluminum chloride, $AlCl_3$, can be changed to aluminum oxide, Al_2O_3, by first precipitating $Al(OH)_3$, using a soluble hydroxide, *e.g.*, NaOH, NH_4OH, and then heating, which aids the decomposition of the hydroxide into the oxide and the volatile substance steam. The two processes are represented by the equations,

$$Al^{+++} + 3\ OH^- = Al(OH)_3,$$

and

$$2\ Al(OH)_3 = Al_2O_3 + 3\ H_2O.$$

To change sodium acid carbonate, $NaHCO_3$ into sodium carbonate, Na_2CO_3 two methods are available. The salt can be dissolved in water and treated with 1 equivalent of NaOH, when the HCO_3^- will be neutralized by the added OH^-, as shown by the equation

$$Na^+ + HCO_3^- + Na^+ + OH^- = 2\ Na^+ + CO_3^{--} + H_2O.$$

The resulting solution yields solid Na_2CO_3 on evaporation. Again, the acid carbonate is capable of another kind of decomposition, represented by the equation,

$$2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Since two of the substances produced by this reaction are volatile, the reaction can be made to proceed so as to produce them by heating the mixture in an open vessel so that they can escape.

To change Na_2CO_3 to NaOH, it is necessary to remove the CO_3^{--} and supply OH^-. Since both sodium compounds are soluble, the insolubility of some other substances must be invoked. We need a hydroxide of some metal which is more soluble than the corresponding carbonate. The best one for this purpose is $Ca(OH)_2$, which is itself scarcely soluble, especially in a solution of NaOH. The insolubility of $CaCO_3$ causes the following reaction to take place, whereas any excess of $Ca(OH)_2$, together with the $CaCO_3$ produced, can be filtered off:

$$Ca(OH)_2 + 2\,Na^+ + CO_3^{--} = CaCO_3 + 2\,Na^+ + 2\,OH^-.$$

Iron rust can be dissolved by moderately dilute hydrochloric acid, as shown by the equation:

$$Fe_2O_3 + 6\,H^+ = 2\,Fe^{+++} + 3\,H_2O.$$

In dissolving a rust or ink stain off a delicate fabric it is not desirable, however, to use such concentrated acid. More dilute H^+ can be used if the reaction is aided by the removal of one of the products. This is accomplished by using oxalic acid, which furnishes both dilute H^+, since it is a rather weak acid, and also oxalic ion, $C_2O_4^{--}$, which unites with the free ferric ion to form a complex ion (see page 185). The reaction is

$$Fe_2O_3 + 6\,H_2C_2O_4 = 2\,Fe(C_2O_4)_3^{---} + 3\,H_2O + 6\,H^+.$$

EXERCISES

1. Under what conditions would you expect the following reactions to take place:

$$CaCO_3 = CaO + CO_2.$$
$$Fe_2(SO_4)_3 + 6\ NaCl = 3\ Na_2SO_4 + 2\ FeCl_3.$$

2. If a solution contains the following ions, how can they be separated: Hg^+, Pb^{++}, Cu^{++}, Ca^{++}?

3. How can the following ions be separated when in the same solution: SO_4^{--}, Cl^-, $C_2H_3O_2^-$, CO_3^{--}?

4. What is formed when ammonia is added, first in small amount, then in excess, to each of the following ions: cupric, zinc, aluminum and silver?

5. Name all the substances present in a dilute solution of sodium acetate, and tell whether each is present in relatively large or small amounts.

6. What class of salts gives an alkaline reaction when dissolved in water, and what class gives an acid reaction? Give examples of each.

7. State which of the following ions would take part in hydrolysis, and write equations for two cases: Cl^-, SO_4^{--}, NH_4^+, Al^{+++}, Ba^{++}, CO_3^{--}.

8. Which of the two salts, NaH_2PO_4 and Na_2HPO_4, would be more hydrolyzed when dissolved in water?

9. Which would be more hydrolyzed, a solution of sodium carbonate or one of sodium acid carbonate of the same molar concentration?

10. What is the effect on a water glass (sodium silicate) solution of (*a*) exposure to the CO_2 in the air; (*b*) the addition of a solution of ammonium chloride?

11. The following substances are relatively insoluble in water; which would dissolve in a solution of HCl? (Give equations and explain your answers.) $Mg(OH)_2$; $BaSO_4$; $CaCO_3$.

12. How would you prepare a pure silver compound and a pure copper compound from a mixture of solid silver chloride and cupric hydroxide? Write equations.

13. In the following list of ions: H^+, Ba^{++}, Ag^+, NH_4^+, SO_4^{--}, Ac^-, Cl^-, CO_3^{--}, CN^-, OH^-, state each pair that would tend to combine largely if brought together in dilute solution. In each case give reason for your answer and write equation.

14. What is an amphoteric substance?

15. Explain the solubility of lead sulfate in (*a*) OH^-; (*b*) Ac^-.

16. Can the following substances be present in moderate concentration in the same solution? If not, what is formed? H^+ and NO_3^-; H^+ and OH^-; H^+ and SO_4^{--}; H^+ and CO_3^{--}; H^+ and $C_2O_4^{--}$; Ca^{++} and CO_3^{--}; Ca^{++} and H_2CO_3; OH^- and H_2CO_3; H_2CO_3 and CO_3^{--}; H^+ and H_2CO_3; HAc and CO_3^{--}; Al^{+++} and OH^-; Cu^{++} and NH_4OH; Cu^{++} and NO_3^-; Ag^+ and NH_3; Hg^{++} and Cl^-.

17. What is the effect of (1) NH_4Cl solution, (2) HNO_3 solution, (3) H_2CO_3 solution, upon a precipitate of $Ca(OH)_2$? Explain in each case.

18. If, when 2 mols of NaCl and 1 mol of H_2SO_4 are brought together, the reaction ceases when the HCl gas produced exerts a pressure of 10 atmospheres at 77° in a volume of 2 liters, (*a*) how many mols each of NaCl and H_2SO_4 have reacted; (*b*) what fraction of each has reacted; (*c*) how might the quantities reacting be increased?

19. How do you account for the fact that antimony sulfide is soluble in concentrated hydrochloric acid, while arsenic sulfide is not?

20. How could you separate arsenic from silver in a mixture of arsenous sulfide and silver sulfide?

21. Which of the precipitates, AgCl, AgI, Ag_2O, Ag_2S, are soluble in (*a*) HNO_3; (*b*) $NH_3 \cdot aq.$; (*c*) CN^-?

22. Cupric hydroxide is readily soluble in ammonia while cupric sulfide is only slightly soluble in the same reagent. Discuss the reactions, and explain the difference in behavior.

23. Starting with metallic calcium, show by means of equations how you would transform it into calcium oxide, the oxide into chloride, chloride into carbonate, and carbonate again into oxide. State, with each reaction, the conditions for carrying it out.

24. Starting with cupric nitrate, how would you prepare in succession: cupric sulfate, cupric oxide, cupric chloride, cupric carbonate, cupric hydroxide?

25. Tell how you would determine, in each of the following cases, whether the impurity named is present or absent. Name reagents used and describe the essential observation in your experiments:

Sulfuric acid in vinegar,
KCl in common salt,
$(NH_4)_2SO_4$ in concentrated H_2SO_4,
Dissolved zinc in a solution of NaOH,
$BaSO_4$ in ZnO.

26. Tell how you would make each of the following transformations, getting the final product as a pure solid. State the reagents used and explain why you would expect your method to work:

NaCl to Na_2SO_4,
$CuSO_4$ to $CuCl_2$,
$Ca^{++} + 2\ HCO_3^-$ to $CaCO_3$,
Na_2CO_3 to NaOH,
$Ag(NH_3)_2^+ + NO_3^-$ to AgCl,
NaOH to Na_2CO_3,
$Zn(NO_3)_2$ to ZnO,
$BaCl_2$ to $Ba(C_2H_3O_2)_2$,
NH_4Cl to NaCl.

CHAPTER XIV

CHEMICAL EQUILIBRIUM. THE EFFECT OF PRESSURE AND TEMPERATURE

When chemical equilibrium has been reached it is possible, as we have seen in the two previous chapters, to bring about a further reaction by altering the concentration of one or more of the reacting substances, which causes that reaction to proceed which will tend to restore the original concentration, or, as we may say, to neutralize the effect of the change. It is likewise possible to affect equilibrium by changing the total pressure to which the system is subject, and by changing its temperature. We will now inquire into the direction in which a reaction must proceed in order to restore equilibrium when subjected to changes in pressure or temperature.

Effect of Changing Total Pressure upon a System in Equilibrium. If we have an equilibrium between a liquid and its vapor, as discussed in Chapter II, we have seen that an increase in the pressure tends to cause vapor to condense, since the number of gaseous molecules is thereby diminished, relieving the pressure We have seen, also, that this is in harmony with the kinetic theory. Now, the same effect is always produced, no matter how complex the equilibrium. An increase in pressure always tends to produce the system having the smallest volume, a decrease in volume tending to relieve the increase in applied pressure. Whenever the total pressure is increased, it increases the concentration

of all of the substances, but this increase in concentration is greatest for those substances having naturally the largest volume. Hence their tendency to react is increased to a greater extent than is that of the substances having a smaller volume, so that the former react more rapidly than the latter, resulting in a shift of equilibrium whereby the set of substances having the largest volume tends to be used up.

Suppose, for example, that we have a closed vessel containing SO_3, SO_2 and O_2 in equilibrium, which has been reached by the substances reacting in one direction or the other, as represented by the equation

$$2\,SO_2 + O_2 = 2\,SO_3.$$

We see from the equation that when SO_3 is formed there is a change in the number of molecules in the proportion 3 to 2. If pressure is applied to the three gases in equilibrium, it will compress them, resulting in a decrease in volume. A further decrease is possible, however, by the union of some of the SO_2 with some of the O_2, and the consequent diminution in the number of molecules, relieving somewhat the pressure applied. Starting, in two experiments, with identical amounts of SO_2 and O_2 at the same temperature, with a catalyst present, or else waiting for equilibrium to be established, we find that more SO_3 will be produced when equilibrium is finally attained if the pressure is high than if it is low.

The same conclusion may be drawn with respect to the reaction

$$N_2 + 3\,H_2 = 2\,NH_3,$$

which shows that ammonia is formed with a diminution in the number of molecules. A high pressure would favor that

reaction which would yield the smallest volume, thus relieving, as far as possible, the high pressure applied.

On the other hand, with the equilibria

$$N_2 + O_2 = 2\,NO, \text{ and } H_2 + Cl_2 = 2\,HCl,$$

with no change in the number of gaseous molecules during a reaction, pressure will be without effect on the amounts formed.

In predicting the effect of pressure we must have regard to the physical states of the substances involved under the conditions of the experiment. It is possible, for instance, by using either liquid sulfur or sulfur vapor to make H_2S directly from its elements. The respective reactions may be represented by the equations

$$H_2 + S\ (\text{liquid}) = H_2S,$$
$$2\,H_2 + S_2\ (\text{vapor}) = 2\,H_2S.$$

In the first reaction there is practically no change in volume, if the reaction is done at constant pressure, as the volume of the liquid sulfur is negligible. Therefore, the relative amounts of H_2 and H_2S present at equilibrium will be practically independent of the pressure applied, or of the volume of the vessel in which the reaction takes place. In the second process, where the conditions are such that the sulfur is in the vapor state, the formation of H_2S at constant pressure results in a decrease in volume, hence the higher the pressure the greater the amount of H_2S formed.

Not only is the effect on the direction indicated by the above discussion, but its magnitude also depends upon the magnitude of the volume change during the reaction. Thus a tenfold increase in total pressure will produce a much greater increase in the amount of NH_3 produced from N_2

and H_2 than in the amount of SO_3 produced from SO_2 and O_2, since the decreases in volume in the two reactions are respectively from 4 to 2 and from 3 to 2. For the same reason very great changes in pressure have to be applied in order to have much effect on equilibria between liquids and solids only, where only small changes in volume occur.

Effect on Equilibrium of Changing the Temperature. In order to appreciate the effect of changing temperature upon a system in equilibrium, we must realize that the immediate effect of any difference in temperature is to determine the flow of heat. If we have a tank of water at 20° C., and put into it a piece of iron at a temperature of 30°, heat will flow from the iron to the water in the tank, tending to equalize the temperature. If, on the other hand, the piece of iron is at a temperature of 10°, when it is put into the water heat will flow from the water into the iron. Suppose, now, that we have a closed vessel containing SO_2, O_2 and SO_3, in equilibrium, in an oven at a temperature of 500°, and we remove it to another oven in which the temperature is 550°. Just as with the piece of iron in the former case, so here heat will flow into the vessel and its reacting mixture. The immediate effect of this heat will be to increase the temperature, the heat content, of the inclosed gases. There is, however, another way in which heat may be absorbed by the mixture, that is, by the reaction proceeding in the direction which absorbs heat. The direction of the reaction for heat absorption is shown by the complete thermochemical equation

$$2\,SO_2 + O_2 = 2\,SO_3 + 45{,}000 \text{ cal.}$$

Since heat is evolved by the formation of SO_3, it will be absorbed by the reverse reaction, in which SO_3 is dissociated

into SO_2 and O_2, hence the effect of bringing the reacting mixture to the higher temperature is to shift the equilibrium so as to form less SO_3.

If, on the contrary, the vessel with its equilibrium mixture is put into an oven at 450°, the heat will flow out of it. This heat will be furnished not only by the cooling of the contained gases, but also by their reacting to some extent to give off heat; accordingly, more SO_3 is present at equilibrium at the lower temperature.

In the formation of NO from its elements heat is absorbed, as shown by the equation

$$N_2 + O_2 = 2\,NO - 44{,}000 \text{ cal.}$$

Consequently, if we have these gases in equilibrium, a rise in temperature will favor the absorption of heat in every possible way, which will not only cause the temperature of the gases to increase, but will also tend to form more NO. We see here that the higher the temperature the more NO will be obtained at equilibrium, while with SO_3 the reverse is true, the higher the temperature the less SO_3 is obtained at equilibrium.

Considerations of this sort apply to every sort of equilibrium and enable us either to predict the effect of changing the temperature from the sign (and magnitude) of the heat of reaction, or, conversely, to predict the latter from the former. As an illustration of this reverse process, let us consider a saturated salt solution where we find that the higher the temperature the more soluble is the salt, and ask ourselves whether this salt evolves or absorbs heat when more dissolves under equilibrium conditions. We have found by experiment that raising the temperature

causes more salt to dissolve. From our theory we conclude that raising the temperature also favors any process that can take place with absorption of heat. Putting these two statements together we conclude that this salt absorbs heat on dissolving, since its solubility increases with the temperature. By similar reasoning, any salt that becomes less soluble as the temperature increases must have positive heat of solution, that is, it must evolve heat on dissolving.

Simultaneous Consideration of All Factors Governing Reactions. In Chapter XI we considered the velocity of chemical reactions, as it is affected by concentration, temperature and the presence of catalysts. We have now considered separately the effect of concentration, pressure and temperature upon chemical equilibrium and are now prepared to consider the simultaneous effect of these factors in controlling chemical reactions. We must again emphasize the fact that the question of velocity is quite distinct from that of equilibrium. If we should put some calcium fluoride, CaF_2, and some calcium sulfide, CaS, into separate beakers of water, we might conclude from a hasty examination that both are very insoluble. As a matter of fact, the small amount of the solid going into solution is due to very different reasons in the two cases. Calcium fluoride is truly insoluble, and no amount of time or stirring would cause more than a very small amount of it to dissolve. On the other hand, calcium sulfide appears to be insoluble because, in order to dissolve, it must hydrolyze, giving $Ca(OH)_2$ and $Ca(SH)_2$, a process which takes place very slowly. Again, calcium chromate, $CaCrO_4$, is more soluble in cold water than in hot, if sufficient time is allowed for the solution to become saturated, but it will dissolve much

faster in hot water than in cold, so that after a given time more might be found in a hot than in a cold solution, although eventually the latter would contain more. It is thus very important, in attempting to realize difficult reactions, to remember that speed and equilibrium are two different considerations, and that conditions which favor the desired equilibrium may not favor its rapid attainment, and vice versa. A discussion of the complete conditions for realizing certain important reactions will make this clearer.

(*a*) **The "Contact Process" for Making Sulfuric Acid.** We have seen above that to make SO_3 from SO_2 and O_2 a low temperature is desirable in order to give the most complete yield of SO_3. By recalling the discussion in Chapter XI, however, we will see that the lower the temperature the more slowly will the desired equilibrium be reached. We must therefore distinguish between the amount of SO_3 which would be produced in infinite time and the amount that would be produced in a given time. This difference may be brought out by the curves in the accompanying figure, Fig. 11, where the heavy line indicates the per cent of the total possible amount of SO_3 which would be obtained at equilibrium, provided that sufficient time were allowed. This time necessary for reaching equilibrium grows enormously as the temperature is lowered, with the result that it is practically impossible to reach equilibrium except at high temperatures, where the amount of SO_2 converted into SO_3 is so small that it would not be profitable to use the reaction. The dotted lines indicate the actual approach to equilibrium in a given time, showing how, by allowing more time, more SO_3 is obtained. At the higher temperatures, such as t_1 and t_2 in the figure, where the reaction

occurs with measurable speed, no amount of waiting will give a satisfactory yield of SO_3. In order to work at temperatures at which the equilibrium is favorable, a new factor must be invoked to increase the velocity. This is attained in practice by the use of catalysts, Fe_2O_3, and finely divided platinum. This allows the desired velocity to be attained

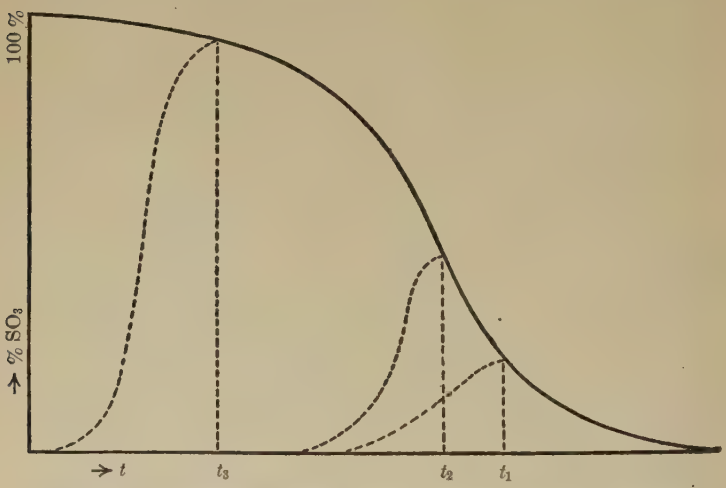


FIG. 11. — Equilibrium between Sulfur Dioxide and Sulfur Trioxide.

at a much lower temperature, t_3 in the figure, where the equilibrium is favorable to a good yield of SO_3. The contact of the gases with this solid catalyst gives the name " contact process." Sulfuric acid is made by dissolving the sulfur trioxide in water.

The speed of the reaction, and also the desired equilibrium, might be influenced in the right direction by having the reaction take place under high pressure. This involves difficulties in the way of more complicated machinery that

it is preferred to avoid in practice. Since the SO_2 must be paid for, while the O_2 is obtained free from the air, it is more important to use up the SO_2 completely than the O_2. This is done by taking the air in considerable excess of the equivalent amount required. We may summarize in tabular form our conclusions concerning the best conditions for realizing this reaction.

	To Favor Large Amount of SO_3 at Equilibrium	To Favor High Speed Either of Formation or Decomposition
Total pressure	High	High
Temperature	Low	High
Other factors	Excess of O_2	Catalyst

To illustrate the conditions to be used in practice, there may be added a table showing the yield of SO_3 that has been calculated, using a gas mixture at a total pressure of 1 atmosphere, with the following partial pressures: SO_2, 0.07 atm.; O_2, 0.10 atm.; N_2, 0.83 atm.

Temperature	434°	550°	645°
Maximum yield, per cent SO_3 .	99	85	60

(*b*) **The Synthesis of Ammonia**. If we compare the reaction for the synthesis of ammonia,

$$N_2 + 3\,H_2 = 2\,NH_2 + 24{,}000 \text{ cal.},$$

with the above reaction for making SO_3, we see that the same conditions are indicated for realizing this reaction as for the former. This reaction, however, is exceedingly slow, so that even with the best catalyst that has been discovered after extensive search, uranium, advantage must be taken of high pressure in aiding both the speed and the

equilibrium at the temperatures at which the reaction will take place with measurable velocity.

The effect of both temperature and pressure on the yield of NH_3 at equilibrium is indicated in the following figures:

Temperature	Yield of NH_3, in Per Cent	
	At 1 atmosphere	At 100 atmospheres
800°	0.011	1.1
700°	0.021	2.1
600°	0.048	4.5
500°	0.13	10.8

A further lowering of temperature below 500° to improve the yield would give too slow a reaction, so that the process is worked at about this temperature, and under pressures up to 200 atmospheres. As the N_2 and H_2 pass over the catalyst they unite partially to form NH_3. The gases are then passed through a cooling coil in which the NH_3 is condensed to liquid and removed. The N_2 and H_2 again pass over the heated catalyst, again forming the equilibrium amount of NH_3 and so on. The removal of NH_3 is compensated by pumping in fresh H_2 and N_2.

This process is now on a working basis and helping to solve the problem of making the inert nitrogen of the atmosphere available for our needs for fertilizer and explosives. It is of interest to note that it was not the discovery of the so-called "practical man," but was the result of extended and difficult scientific research along the lines here indicated. The conditions employed are such as would not occur to one not well versed in the theory, and call for pressures such as were never before used in a similar process.

(*c*) **The Synthesis of Nitric Oxide.** We have already referred briefly to the reaction,

$$N_2 + O_2 = 2\,NO - 44{,}000 \text{ cal.}$$

We see that the formation of NO would be aided by the following conditions, which we will tabulate as before.

	To Favor Large Amount of NO at Equilibrium	To Favor High Speed Either of Formation or Decomposition
Total pressure	No effect	High
Temperature	High	High

As a consequence of these conclusions, we see that NO should be formed more rapidly and also more completely at high temperatures. That this is true is seen from the following figures on the basis of experiments:

Per cent NO at equilibrium, starting with air .	0.37	0.97	5.0	10
Temperature	1540	1920	2930	3930

Obviously NO is only stable, in a true sense, at extremely high temperatures, and both a favorable equilibrium and high speed in attaining it are aided by high temperatures such as those given by an electric arc. The problem is then to get it down to ordinary temperature without letting the equilibrium shift back to N_2 and O_2 as it cools. This is done by cooling it sufficiently rapidly as the gas mixture leaves the arc. There is also an electrical effect, due to the arc, tending to give a greater yield than is indicated by the above conditions of ordinary equilibrium.

At ordinary temperatures NO unites with more O_2 readily to form N_2O_4, which will also dissolve in water, forming a mixture of nitric and nitrous acids. The N_2O_4 may also be

passed over slaked lime, giving a mixture of calcium nitrite and nitrate, which is used as fertilizer to supply nitrogen to the soil. This process was first used successfully on a commercial scale in Norway, and is now responsible for the fixation of enormous quantities of nitrogen.

(*d*) **The "Cracking" of Petroleum.** The principles above set forth have been of great aid in "cracking" the heavier constituents of petroleum so as to increase the yield of the more valuable lighter portions, such as benzene, C_6H_6, toluene, $C_6H_5CH_3$, and those like C_5H_{12}, C_6H_{14}, C_7H_{16}, etc., which are contained in gasolene. It has been found possible to control the nature of the products to a remarkable degree by designing apparatus that would permit of the independent control of temperature and pressure. The same substance is capable of a number of different transformations which would be influenced in different ways by changing the pressure and temperature. The probable effect of these factors may be predicted by the aid of the complete equations showing both the volume changes and the heats of reaction. The subject is too complicated for further discussion here, and we will merely give for illustration several equations showing possible reactions for $C_{12}H_{26}$, a prominent constituent of kerosene.

$$2\,C_{12}H_{26} = CH_4 + C_{23}H_{48} - 500 \text{ cal.},$$
$$C_{12}H_{26} = C_2H_2 + 2\,C_5H_{12} - 47{,}000 \text{ cal.},$$
$$C_{12}H_{26} = 6\,C_2H_2 + 7\,H_2 - 381{,}000 \text{ cal.},$$
$$3\,C_2H_2 = C_6H_6 + 137{,}700 \text{ cal.}$$

It is evident that the equilibria in these reactions would be influenced in very different ways by pressure and temperature.

EXERCISES

1. If the volume of a solution is greater than that of the salt and water from which it is made, how will the solubility of the salt change when pressure is applied to the saturated solution?

2. In which direction would each of the following equilibria be displaced by decreasing the total pressure: (Explain.)

$$N_2O_4 = 2\ NO_2,$$
$$2\ HCl = H_2 + Cl_2,$$
$$C\ (\text{solid}) + S_2\ (\text{vapor}) = CS_2\ (\text{vapor}).$$

3. Ammonium chloride dissolves with considerable absorption of heat. How is its solubility affected by the temperature?

4. The solubility of sodium chloride increases very slightly with temperature. What can be concluded concerning its heat of solution?

5. When AgCl is prepared by mixing its ions heat is evolved. Is the precipitate more soluble in hot or in cold water? (Explain.)

6. Explain how temperature would affect the production of H_2S according to the reaction:

$$H_2 + S = H_2S + \text{heat}.$$

7. The formation of benzene from acetylene according to the reaction $3\ C_2H_2 = C_6H_6 + 131{,}000$ cal. takes place slowly at a high temperature (benzene being a vapor) and is reversible.

(*a*) What weight of benzene could be made by the complete conversion of 49.3 liters of acetylene, measured at 27° C. and 1 atmosphere?

(*b*) State and explain the experimental conditions you would adopt to secure the maximum yield of benzene from acetylene in a given time.

8. Is the peculiar taste of stale bread due to its becoming dry? Why do crackers taste fresh as long as they are kept dry? How can the fresh taste be restored in either bread or crackers? Would bread keep fresh longer in a refrigerator than at room temperature?

CHAPTER XV

OXIDATION AND REDUCTION

In the previous chapters our attention has been largely confined to reactions in which there are no changes in valence. In Chapter V, however, brief mention was made of reactions in which such changes do occur, and it was there pointed out that oxidation consists essentially of an increase of valence, and reduction of a decrease of valence. We are now prepared to give fuller attention to such reactions, considering, first, the writing of equations representing them, and, second, the oxidizing and reducing powers of the substances involved.

Whenever an element is oxidized some element must be reduced. The substance containing the element which is oxidized is called the **reducing agent**, since it is responsible for the reduction of the other element. Conversely, the substance which causes an increase in valence is the **oxidizing agent**, and contains an element which is reduced. The following table illustrates these terms:

$$Cu + 2\,H_2SO_4 = CuSO_4 + SO_2 + 2\,H_2O.$$

Valences 0 6 2, 6 4

Element oxidized, Cu. Oxidizing agent, H_2SO_4.

Element reduced, S. Reducing agent, Cu.

$$H_2S + I_2 = S + 2\,H^+ + 2\,I^-.$$

Valences 1, − 2 0 0 − 1

Element oxidized, S. Oxidizing agent, I_2.

Element reduced, I. Reducing agent, H_2S.

$$2\,Fe^{+++} + H_2SO_3 + H_2O = 2\,Fe^{++} + SO_4^{--} + 4\,H^+$$

Valences 3 4 2 6

Element oxidized, S. Oxidizing agent, Fe^{+++}.

Element reduced, Fe. Reducing agent, H_2SO_3.

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ = Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$

Valences 7 2 2 3

Element oxidized, Fe. Oxidizing agent, MnO_4^-.

Element reduced, Mn. Reducing agent, Fe^{++}.

Writing Equations for Reactions Involving Oxidation and Reduction. (*a*) **The Substance Produced.** Before an equation can be written for any reaction it is necessary to know what substances are produced. This may be determined by experiment or predicted, in most cases, from a knowledge of the reacting substances. For example, when hot concentrated sulfuric acid reacts with copper it is possible to detect the evolution of sulfur dioxide by its odor, and the production of copper sulfate by the blue color it gives on the addition of water. When sulfurous acid acts upon ferric ion, the ferrous ion produced shows its presence by its faint green color, or by other characteristic tests, and the formation of sulfate ion can be proved by adding barium ion. One sufficiently familiar with the chemistry of iron and of sulfur would not need these tests, for he knows that when ferric ion decreases in valence in acid solution it usually becomes ferrous ion, and that the corresponding increase of valence on the part of sulfurous acid would give sulfate ion. It is therefore important to know the valences the elements are capable of assuming and the compounds characteristic of each valence.

For example, many of the metals, including the alkali and alkaline earth metals, silver, zinc, cadmium and aluminum, exhibit only one valence in addition to that of the free metal, which is zero. Therefore a substance like aluminum ion, Al^{+++}, cannot be oxidized farther, nor can it be reduced to metal in water solution. Hence we would not expect it to take part in any oxidation or reduction process in aqueous solution. Chlorine shows the following valences, -1, 0, $+1$, $+3$, $+5$, $+7$, which correspond to the compounds tabulated on page 100. Consequently, we would never find the chlorine in chloride ion, Cl^-, acting as an oxidizing agent, because it is already as completely reduced as it is capable of being. Likewise, if chlorine, Cl_2, acts as an oxidizing agent it must be reduced, and the only possible product would be chloride ion or one of its compounds. Again, knowing that chlorine reacts with hydroxide ion as follows:

$$Cl_2 + 2\,OH^- = Cl^- + ClO^- + H_2O,$$

we know that when ClO^- acts as an oxidizing agent in alkaline solution, the chlorine could not be reduced to the next lower valence, zero, corresponding to Cl_2, but would be reduced all the way to chloride ion.

The following table represents the substances characteristic of chromium in the valences of three and six respectively, and in acid, neutral or alkaline solution:

	Acid	Neutral	Alkaline
Valence 3	Cr^{+++}	$Cr(OH)_3$	CrO_2^-
Valence 6	$Cr_2O_7^{--}$	CrO_4^{--}	CrO_4^{--}

In accordance with the knowledge thus summarized, we would expect Cr^{+++} to be produced when a reducing agent acts upon $Cr_2O_7^{--}$. Similar information should be remembered for the other common elements giving compounds in which they show more than one valence.

(*b*) **The Assignment of Valence Numbers to the Elements Oxidized and Reduced.** Having decided upon the substances produced by the reaction, the first step is to write their formulas, together with those of the substances reacting, upon the appropriate side of the equation, and to assign a valence number to the elements oxidized and reduced, as explained in Chapter V. Let us illustrate the process by balancing the equations given in the preceding table. Omitting the valence numbers for the elements obviously not oxidized or reduced during the reaction we would have the following incomplete equations:

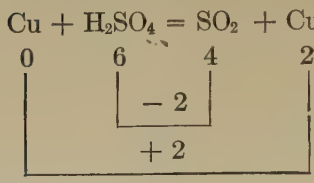
$$\begin{array}{cccccc} Cu & + & H_2SO_4 & = & SO_2 & + & CuSO_4. \\ 0 & & 6 & & 4 & & 2 \end{array}$$

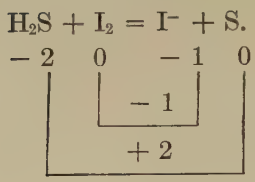
$$\begin{array}{cccccc} H_2S & + & I_2 & = & I^- & + & S. \\ -2 & & 0 & & -1 & & 0 \end{array}$$

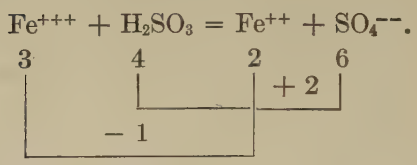
$$\begin{array}{cccccc} Fe^{+++} & + & H_2SO_3 & = & Fe^{++} & + & SO_4^{--}. \\ 3 & & 4 & & 2 & & 6 \end{array}$$

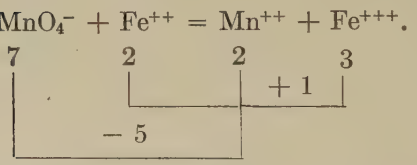
$$\begin{array}{cccccc} MnO_4^- & + & Fe^{++} & = & Mn^{++} & + & Fe^{+++}. \\ 7 & & 2 & & 2 & & 3 \end{array}$$

(*c*) **The Determination of the Change in Valence per Atom of Each Element Oxidized and Reduced** is the next step. This may be conveniently indicated by marking it upon a line connecting the elements in question, as follows:









(*d*) **The next step is the adjustment of the molecules of these substances so that the total increase in valence of the atoms oxidized equals the total decrease in valence of the atoms reduced.** In the first equation it is seen that the production of one molecule of SO_2 will correspond to the oxidation of one atom of copper, hence no further change is necessary under this heading.

In the second, obviously, one atom of sulfur can oxidize two atoms of iodine, so that this equation should be altered to read

$$H_2S + I_2 = 2\,I^- + S.$$
$$-2 \quad 0 \quad 2(-1) \quad 0$$
$$2(-1)$$
$$+2$$

In the third, two atoms of iron can be reduced when one atom of sulfur is oxidized, so that we should write:

$$2\,Fe^{+++} + H_2SO_3 = 2\,Fe^{++} + SO_4^{--}.$$
$$2(3) \quad 4 \quad 2(2) \quad 6$$
$$+2$$
$$2(-1)$$

In the fourth, every atom of manganese, in being reduced, can oxidize five atoms of iron, hence we write:

$$MnO_4^- + 5\,Fe^{++} = Mn^{++} + 5\,Fe^{+++}.$$
$$7 \quad 5(2) \quad 2 \quad 5(3)$$
$$+5$$
$$-5$$

(*e*) **The final balancing of the equation** usually requires the addition to one side or the other of appropriate substances. Thus, in the first example it is evident that another molecule of sulfuric acid is needed on the left to furnish the sulfate radical for the copper sulfate, so that we will have

$$Cu + 2\,H_2SO_4 = SO_2 + CuSO_4.$$

Now we have four atoms of hydrogen and two extra atoms of oxygen on the left which must be balanced by adding $2\,H_2O$ on the right, so that the completed equation will be

$$Cu + 2\,H_2SO_4 = SO_2 + CuSO_4 + 2\,H_2O.$$

It is desirable to test the accuracy with which the above steps have been made by seeing if the total number of atoms of each element on one side of the equation equals that on the other.

In the second equation, we see that we have, so far, two atoms of hydrogen on the left, and two negative charges on the right, with no counterpart on the other side. By adding on the right two hydrogen ions the equation will obviously be balanced, reading finally as follows:

$$H_2S + I_2 = 2\,I^- + S + 2\,H^+.$$

In the final testing of an equation like this the total charges on the two sides, canceling those of opposite sign, must be the same.

In the third equation, we have one atom of oxygen in excess on the right, and two atoms of hydrogen and four positive charges in excess on the left. In such cases probably it is simplest to balance the charges first, by adding to one side or the other the proper amount of H^+ or OH^-. In the above instance the charges could obviously be balanced either by adding $4\,H^+$ on the right or $4\,OH^-$ on the left. Either would enable us to balance the equation, but from a chemical standpoint it would be incorrect to add $4\,OH^-$, for the solution is not alkaline, since Fe^{+++} and H_2SO_3 are unable to exist in alkaline solution. Accordingly, we add $4\,H^+$ on the right, whereby the equation becomes

$$2\,Fe^{+++} + H_2SO_3 = 2\,Fe^{++} + SO_4^{--} + 4\,H^+.$$

All that is necessary now, finally to balance the equation, is to add H_2O on the left, getting

$$2\,Fe^{+++} + H_2SO_3 + H_2O = 2\,Fe^{++} + SO_4^{--} + 4\,H^+.$$

In the fourth case, evidently an acid solution likewise, it is necessary, in order to balance the charges, to add 8 H^+ on the left, getting

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ = Mn^{++} + 5\ Fe^{+++}.$$

This requires only the addition of 4 H_2O on the right to become complete.

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ = Mn^{++} + 5\ Fe^{+++} + 4\ H_2O.$$

As an example of balancing an equation for a reaction occurring in alkaline solution we may take the following, where the steps just explained are indicated successively.

(*a*) $CrO_2^- + ClO^- = Cl^- + CrO_4^{--}$.

(*b*) 3 1 −1 6

(*c*) −2; +3

(*d*) $2\ CrO_2 + 3\ ClO^- = 3\ Cl^- + 2\ CrO_4^{--}$.
2 (3) 3 (1) 3 (−1) 2 (6)
3 (−2); 2 (+3)

(*e*) $2\ CrO_2^- + 3\ ClO^- + 2\ OH^- = 3\ Cl^- + 2\ CrO_4^{--}$.
$2\ CrO_2^- + 3\ ClO^- + 2\ OH^- = 3\ Cl^- + 2\ CrO_4^{--} + H_2O$.

The Relative Oxidizing and Reducing Powers of Various Substances.

(*a*) **The Metals and Their Ions.** It was pointed out in Chapter V that the more positive elements can replace the less positive ones in their compounds. This is illustrated by the following reactions, all of which take place quite readily:

$$2\,Na + Zn^{++} = Zn + 2\,Na,$$
$$Zn + Fe^{++} = Fe + Zn^{++},$$
$$Fe + Pb^{++} = Pb + Fe^{++},$$
$$Pb + Cu^{++} = Cu + Pb^{++},$$
$$Cu + 2\,Hg^{+} = 2\,Hg + Cu^{++},$$
$$Hg + Ag^{+} = Ag + Hg^{+}.$$

In each of these cases the baser metal is oxidized by the ion of the nobler one, and it is evident that zinc will reduce not only ferrous ion, but lead, copper and silver ions as well. Likewise, silver ion can act as an oxidizing agent, not only to copper, but to all of the other metals represented. In all cases the metals act as the reducing agents, their reducing power decreasing as we descend the list, while the ions act as oxidizing agents, their oxidizing power increasing as we descend the list. This behavior may be summarized in the following table:

Oxidation								Reduction
↑	Weak		Oxidizing Agents			Strong		↓
	Na^{+}	Zn^{++}	Fe^{++}	Pb^{++}	Cu^{++}	Hg^{+}	Ag^{+}	
	Na	Zn	Fe	Pb	Cu	Hg	Ag	
	Strong		Reducing Agents			Weak		

This table has been arranged so that any ion will be reduced if brought in contact with a metal to the left in the table. In order, however, for this arrangement to hold, the ions must all be in approximately equal concentration. If this is not the case, the positions of some may be reversed. Thus Hg^{+} and Ag^{+} have about the same oxidizing power, hence the reaction

$$Hg^{+} + Ag = Ag^{+} + Hg$$

is easily reversible by changing the relative concentrations. The principles of equilibrium set forth in Chapter XII apply

here also, so that a high concentration of Hg^+ and a low concentration of Ag^+ favor the reaction as read from left to right, whereas the reverse reaction is favored by reversing the relative concentrations. With most pairs of metals the corresponding reversal requires greater differences in concentration.

Many interesting applications of this oxidation-reduction series are possible. For example, it is evident that if a piece of zinc is put into a solution of ferrous ion there is a tendency for the latter to be reduced. Accordingly, if zinc and iron are in contact in an oxidizing solution, the former will be dissolved before the latter. This is the reason for the protective action of the zinc coating on "galvanized" iron.

When a piece of zinc is dropped into a solution of one of the ions to the right of it in the table, a reaction takes place such as the following:

$$Zn + Cu^{++} = Cu + Zn^{++}.$$

Now this may be regarded as a transfer of positive electricity from the copper ion to the zinc, or, better, as the transfer of negative electrons from the zinc to the copper ion. If this transfer of electricity can be made to take place through a wire we will have an electric current, and the reaction can be made to do work. To do this the zinc must not be put directly into the solution of copper ion, but electrodes of the two metals must dip into solutions of their own ions, the solutions being separated by a porous partition or by the aid of their difference in density, as in the case in the well-known "gravity cell." At the zinc electrode the following process tends to take place:

$$Zn = Zn^{++} + 2\,(-),$$

while at the copper electrode the reaction is

$$Cu^{++} + 2(-) = Cu.$$

Each of these processes can continue only if the stream of negative electrons, or atoms of electricity, can flow from the zinc to the copper, while the positive and negative ions in the solution migrate towards their respective poles. For every mol of zinc that dissolves one mol of copper will be deposited and two faradays of electricity (see page 129) will travel through the wire. The electromotive force between the electrodes depends upon the difference between the tendencies of the metals to become ions, and also upon the relative concentration of the ions in the solution. If the concentration of zinc ion is diminished, or that of copper ion is increased, the reaction

$$Zn + Cu^{++} = Cu + Zn^{++}$$

will have a greater tendency to take place, and will give a larger electromotive force when occurring in an electric battery. If silver ion and silver are substituted for copper ion and copper, we will have a stronger oxidizing agent, a greater tendency to take up the electrons given off by the zinc and a battery of higher electromotive force.

The electromotive force of such a battery is thus a measure of the tendency of the reaction to take place, or the **chemical affinity** of the reaction, a term much used in the development of chemistry, but also much abused, for it has often been used very loosely. It is only in comparatively recent years that it has been given an exact definition. On this account it is desirable to substitute the term "**free energy**" for affinity. The electromotive force of the copper-

zinc cell when normal solutions of copper and zinc sulfates are used is about 1.09 volts. The free energy of the reaction at these concentrations is the work it can do, which would be $1.09 \times 2 \times 96540$ volt-coulombs, or joules, per mol of reacting substances.

The reaction between zinc and silver ion may be utilized in cleaning the tarnish from silverware. The tarnish consists of silver sulfide, Ag_2S, and though this gives but a small concentration of silver ion, the free energy of the reaction is still sufficient for it to take place quite readily. If, therefore, a piece of zinc (aluminum will also serve) is placed in electrical contact with a piece of tarnished silver, both dipping into water containing a little salt to render it conducting, and hot to increase the speed of reaction, the following reaction takes place:

$$Ag_2S + Zn = 2\,Ag + Zn^{++} + S^{--}.$$

The silver is thus restored instead of being rubbed off as in ordinary polishing.

If a solution containing the ions of two metals is electrolyzed, it is possible to reduce at the cathode, first the ion of the nobler metal, and afterwards that of the baser metal, by proper regulation of the electromotive force. It is possible thus to make an electrolytic separation of different metals which is to be preferred, in many cases, to the ordinary methods of separation based upon the precipitation of insoluble compounds.

(*b*) **The Solubility of Metals in Water, Acids and Alkalis.** When a metal dissolves in water, in alkali, or in dilute acids the substance reduced is usually hydrogen ion. Accordingly, it is desirable to introduce H^+ and H_2 into the table

previously given. In attempting to do this we find an apparent discrepancy in the reactions of the metals with hydrogen ion, for iron will dissolve in dilute hydrogen ion, whereas zinc, if very pure, and especially if wet with mercury, will not. We find, however, that this is due to the difficulty which hydrogen has in depositing on a surface of pure zinc or mercury, for if a piece of platinum is dipped into the acid and brought into contact with the zinc, we find that the latter dissolves quite readily. The hydrogen is deposited on the platinum, while the electrons left behind when zinc is converted to zinc ion, travel through the metals to the platinum, where they neutralize the hydrogen ions, changing them into hydrogen gas. If we test the solubility of the various metals in dilute acids in this way, we find that all those to the left of copper in the table will dissolve, although lead and zinc will do so only with great difficulty, when pure, and in the absence of some more favorable surface for the hydrogen to deposit upon. The same difficulty is encountered in reducing hydrogen ion at certain cathodes, for a higher electromotive force is required to deposit hydrogen at a certain rate on some surfaces than on others. A successively higher electromotive force is required with cathodes of the following substances: Pt (rough), Pt (smooth), Ag, Cu, Sn, Pb, Zn, Hg. Hydrogen thus takes the place given in the more extended table on page 242, provided that a rough platinum surface is in electrical contact with the metal dissolving. We see, then, that copper, silver, mercury and the other noble metals will not dissolve in acids like dilute hydrochloric and sulfuric under any circumstances, while lead and the baser metals will dissolve in dilute hydrogen ion, provided that platinum is in contact with the

metal, but that lead and zinc, or other base metals if amalgamated with mercury, may dissolve very slowly, or practically not at all. When impure zinc is used, the particles of foreign substances, like iron and carbon, furnish nuclei upon which the hydrogen can deposit with more ease, hence such zinc will dissolve at a reasonable rate.

As we approach the left side of the table, where the metals become baser, and better reducing agents, the hydrogen ion does not need to be so concentrated in order to act upon the metal, and even the extremely dilute hydrogen ion of water is able to oxidize and dissolve metals like calcium and sodium.

Aluminum dissolves easily in dilute hydrogen ion, the reaction being

$$Al + 3\,H^+ = Al^{+++} + \tfrac{3}{2}\,H_2.$$

If hydroxide ion is used instead of hydrogen ion, although the decrease in the concentration of the latter would tend, by itself, to stop the solution of the aluminum, at the same time the concentration of aluminum ion is decreased very greatly on account of the formation of the aluminate ion, a fact which aids the reaction, and compensates for the reduction in the hydrogen ion concentration. Hence aluminum will dissolve in alkali as well as in acid. The same is true of zinc.

For the metals to the right of hydrogen in the table a stronger oxidizing agent than hydrogen ion is necessary. This is found, for some, in nitric acid, whose oxidizing action is due to the reduction of nitrogen rather than of hydrogen. Copper, silver and mercury can accordingly be dissolved in nitric acid. A typical reaction is the following:

$$3\,Cu + 2\,NO_3^- + 8\,H^+ = 3\,Cu^{++} + 2\,NO + 4\,H_2O.$$

Sulfuric acid, if hot and concentrated, can oxidize copper, silver and mercury, its sulfur being reduced to SO_2.

When we come to the noblest metals, like gold and platinum, even the oxidizing power of nitric acid becomes insufficient. Instead, however, of seeking a stronger oxidizing agent, another principle is invoked. The following reaction will not take place with nitric acid alone:

$$2\,Pt + 4\,NO_3^- + 16\,H^+ = 2\,Pt^{++++} + 4\,NO + 8\,H_2O.$$

Platinic ion, however, is prone to form a complex acid with hydrochloric acid, H_2PtCl_6, chlor-platinic acid (see page 185), and hence, if a mixture of hydrochloric and nitric acids, known as "aqua regia," is used instead of the nitric acid alone, the platinic ion, one of the products of the oxidation, is used up sufficiently to enable the reaction to proceed. This action of aqua regia is not due, as is often erroneously stated, to the fact that the chlorine liberated by the aqua regia ($4\,H^+ + NO_3^- + 3\,Cl^- = Cl_2 + NOCl + 2\,H_2O$) is a stronger oxidizing agent than the nitric acid, for if this were the case chloride ion would not be oxidized by nitric acid. Chlorine is, however, a more **rapid** oxidizing agent, and the effectiveness of the aqua regia is doubtless due to this fact as well as to the formation of the complex chlor-platinic acid. The action of aqua regia on gold is quite analogous to that on platinum. In this case the complex chlor-auric acid, $HAuCl_4$, is formed.

Cyanide ion, CN^-, forms such a firm complex with both aurous and auric ions that when it is present the oxygen of the air is sufficient to oxidize gold; the reaction is

$$2\,Au + \tfrac{1}{2}\,O_2 + H_2O + 4\,CN^- = 2\,Au(CN)_2^- + 2\,OH^-.$$

This reaction is used in the "cyanide process" for the extraction of gold from its ores.

(*c*) **General Table of Oxidizing and Reducing Agents.** We may consider the oxidizing and reducing powers involved in changes other than those between the metals and their ions just considered. We find, for example, that chlorine will liberate bromine from bromide ion, and that bromine will liberate iodine from iodide ion. Accordingly, we may conclude that chlorine will liberate iodine from iodine ion. This information may be tabulated in the same way as was used previously for the metals, as follows:

Weak	Oxidizing Agents	Strong
I_2	Br_2	Cl_2
I^-	Br^-	Cl^-
Strong	Reducing Agents	Weak

By the aid of appropriate experiments we may find the place of other common substances in such a table, and also combine it with the table previously given. The following table gives an illustration of such arrangement.

TABLE OF OXIDIZING AND REDUCING POWERS OF SUBSTANCES

		Oxidation →	
Strong	Zn		Zn^{++}
	Fe		Fe^{++}
	Sn		Sn^{++}
	Pb		Pb^{++}
	H_2 on Pt		H^+
	Sn^{++}		Sn^{++++}
Reducing Agents	H_2S only →		S
	SO_2 only →		SO_4^{--}
	I^-		I_2
	Fe^{++}		Fe^{+++}
	Ag		Ag^+
	Br^-		Br_2
	I_2		IO_3^-
	SO_2		H_2SO_4, hot concentrated
	NO only ←		HNO_3
	Cr^{+++}		$Cr_2O_7^{--}$ + conc. H^+
Weak	Mn^{++}		MnO_4^- + H^+
	Pb^{++}		PbO_2 + concentrated H^+ (HNO_3)
		Reduction ←	

Weak — Oxidizing Agents — Strong

It should be borne in mind that such an arrangement is not altogether rigid, and that it is affected by the concentrations of the reacting substances. According to the table, for example, one might infer that the following reaction would occur:

$$Ag^+ + I^- = Ag + \tfrac{1}{2} I_2.$$

This would undoubtedly take place if Ag^+ and I^- could act upon each other at ordinary concentrations without precipitating insoluble AgI. The same applies to the action of H_2S on Ag^+.

The hydrogen ion concentration affects the equilibrium in many cases. For example, the reaction

$$SO_2 + I_2 + H_2O = SO_4^{--} + 2\,I^- + 4\,H^+$$

proceeds readily in dilute solution. It will be seen, however, that by diminishing the amount of water present and increasing the relative amount of acid the equilibrium is shifted in favor of those substances on the left, and, as a matter of fact, concentrated sulfuric acid readily liberates iodine from solid iodides. Similarly, the following reaction accords with the positions in the table of the substances involved:

$$Cr_2O_7^{--} + 6\,Cl^- + 14\,H^+ = 2\,Cr^{+++} + 3\,Cl_2 + 7\,H_2O,$$

and in concentrated acid the reaction proceeds in this way. The large amount of H^+ used up, however, indicates that the equilibrium would be enormously affected by changing its concentration. In fact the reaction proceeds in the other direction in alkaline solution, the chromium being oxidized and the chlorine reduced. The transition from one to the other may be made by adding 16 OH^- to both sides of the equation. Of these, 14 OH^- will react with the 14 H^+,

2 OH^- with $Cr_2O_7^{--}$ giving 2 CrO_4^{--} + H_2O, and on the right we will have 2 Cr^{+++} + 8 OH^- = 2 CrO_2^- + 4 H_2O, and 3 Cl_2 + 6 OH^- = 6 ClO^- + 3 H_2O, with 2 OH^- in excess. Canceling out H_2O and Cl^-, and transposing the two sides, we have the equation previously considered on page 233.

$$2\ CrO_2^- + 3\ ClO^- + 2\ OH^- = 3\ Cl^- + 2\ CrO_4^{--}.$$

Although this is apparently very different from the equation given above, it involves essentially the same oxidation and reduction steps. On account of the great effect on many of these reactions of varying the concentration of the ions of water, it is well to include in a separate table the reagents which act in alkaline solution. The following brief table may serve for illustration:

Weak	Oxidizing Agents	Strong
$HSnO_3^-$	CrO_4^{--}	ClO^-
$HSnO_2^-$	CrO_2^-	Cl^-
Strong	Reducing Agents	Weak

Oxidizing Power and Speed of Oxidation. There are some substances, like hydrogen peroxide, H_2O_2, which would have great oxidizing power if they could react rapidly enough. It is important to distinguish between an oxidizing agent that is " strong " because it is rapid, and one which is strong but slow. Thus iodine will often react more rapidly than chlorine, and hence produce more oxidation in a given time. Its true oxidizing power, however, is much less, as shown by the fact that it will not oxidize ferrous ion completely, whereas chlorine will. The oxygen acids, like nitric and sulfuric acids, are not rapid oxidizing agents. This seems to be connected with the fact that they are highly ionized.

Nitrous acid, which is not a stronger oxidizing agent in the true sense of the term, is nevertheless a much more rapid oxidizing agent, and is, at the same time, much less dissociated. As we compare the oxygen acids of chlorine, we find that while their reactivity as oxidizing agents decreases in going from $HClO$ to $HClO_3$, their strength as acids increases greatly. In a reaction such as the following,

$$ClO_3^- + S + H_2O = Cl^- + SO_4^{--} + 2\,H^+,$$

although hydrogen ion appears, whence we might expect it to be favored by decreasing the concentration of hydrogen ion, as a matter of fact it will not take place unless the solution is strongly acid. We may infer from this that ClO_3^- is very unreactive, and a large amount of H^+ must be present in order to give a certain amount of the undissociated strong acid, $HClO_3$, which is reactive. With $HClO$, however, reduction to Cl^- will take place rapidly without adding H^+, because $HClO$ is such a weak acid that most of it is undissociated even in neutral solution. The difference between nitrous and nitric acids may be explained similarly; the latter, being a strong acid, must be rather concentrated in order to give enough undissociated molecules of HNO_3 to react rapidly. In general, when substances react slowly their true place in the table may not be apparent from their ordinary reactions, and the place assigned may not correspond to a reversible reaction.

Substances That Can Act Both as Oxidizing and Reducing Agents. Certain substances appear at two places in the table, corresponding to their power to act either as oxidizing or reducing agents. The way in which they will react depends, of course, upon the nature of the substances with

which they are mixed. Thus ferrous ion can be reduced to iron by the action of a very powerful reducing agent like zinc, or it can be oxidized to ferric ion by the action of a strong oxidizing agent like chlorine. Iodine may be reduced to iodide or oxidized to iodate according, respectively, as it reacts with a reducing agent stronger than iodine or an oxidizing agent stronger than iodate ion. Hydrogen peroxide, not shown in the table because of the irreversibility and slowness of its reactions, may act as an oxidizing agent with some substances themselves capable of oxidation. In these cases the oxygen in the hydrogen peroxide is reduced, as illustrated by the reaction

$$2\,H^+ + H_2O_2 + 2\,Fe^{++} = 2\,Fe^{+++} + 2\,H_2O.$$

On the other hand, in the presence of a sufficiently strong oxidizing agent, the oxygen in the peroxide may be oxidized to free oxygen, as illustrated by the reaction

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ = 2\,Mn^{++} + 5\,O_2 + 8\,H_2O.$$

The Solution of Insoluble Sulfides. In Chapter XIII it was shown how certain metallic sulfides could be separated by controlling the hydrogen ion concentration, and it was pointed out that there is a group of sulfides so insoluble in water that even moderately concentrated hydrochloric or sulfuric acids will not sufficiently remove the sulfide ion, S^{--}, to make the metallic ion concentration large. To dissolve such sulfides it is necessary to remove the sulfide ion more completely. This is possible by the use of a strong oxidizing agent, usually nitric acid, which changes the S^{--} completely into S or even SO_4^{--}. Moderately concentrated hot nitric acid, accordingly, will dissolve CuS, Bi_2S_3, PbS and Ag_2S.

The solubility of mercuric sulfide is so extremely low, however, that nitric acid is practically without effect. To dissolve it aqua regia is necessary, the effectiveness of which depends upon the greater speed of reaction of chlorine as compared with nitric acid, and also upon the presence of the chloride ion, which unites with the mercuric ion to form undissociated mercuric chloride. The aqua regia thus attacks both constituents of the mercuric sulfide instead of only one.

Storage Batteries. Other reactions besides the simple change between metals and their ions can be utilized in generating an electric current. A very important one is that occurring in the lead storage battery. The reaction utilized is the following:

$$Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{--} = 2\,PbSO_4 + 2\,H_2O.$$

It is carried out so that the oxidation of the lead to lead sulfate,

$$Pb + SO_4^{--} = PbSO_4 + 2\,(-),$$

takes place at one electrode and the reduction of lead dioxide to lead sulfate,

$$PbO_2 + 4\,H^+ + SO_4^{--} + 2\,(-) = PbSO_4 + 2\,H_2O,$$

takes place at the other electrode. The electrons travel through the metallic part of the circuit from one electrode to the other. To charge the cell the reaction is reversed by sending a current through the cell in the opposite direction. From the equations it may be seen that the more concentrated is the acid the more is the equilibrium shifted in favor of $PbSO_4$, hence the larger the free energy of the reaction and the electromotive force of the cell. There are other

considerations, however, which we have not room to consider here, which argue against too concentrated an acid.

The nickel-iron storage battery utilizes the following reaction, taking place in alkaline solution:

$$2\ Ni(OH)_3 + Fe = 2\ Ni(OH)_2 + Fe(OH)_2.$$

The electrode reactions are

$$2\ Ni(OH)_3 + 2\ (-) = 2\ Ni(OH)_2 + 2\ OH^-,$$

and

$$Fe + 2\ OH^- = Fe(OH)_2 + 2(-).$$

EXERCISES

1. In the following reactions state which elements are oxidized and which are reduced:

$$2\ Ag^+ + Zn = 2\ Ag + Zn^{++};$$
$$Ag^+ + Cl^- = AgCl;$$
$$Zn + OH^- + H_2O = HZnO_2^- + H_2;$$
$$2\ Hg^+ + H_2S = HgS + Hg + 2\ H^+;$$
$$2\ HgCl_2 + Sn^{++} = 2\ HgCl + Sn^{++++} + 2\ Cl^-.$$

2. Write equations for the following reactions: zinc plus chlorine to give zinc ion plus chloride ion; stannous ion plus bromine to give stannic ion plus bromide ion; ferric ion plus stannous ion to give ferrous ion plus stannic ion; hydrogen sulfide (H_2S) plus iodine to give sulfur plus hydrogen ion plus iodide ion; cupric ion plus iodide ion to give cuprous iodide (ppt.) plus iodine.

3. Write equations for the reactions between: (*a*) cupric oxide and hydrogen; (*b*) cupric oxide and hydrogen ion; (*c*) cuprous oxide and oxygen; (*d*) magnesium and hydrogen ion; (*e*) cupric ion and zinc to give copper; (*f*) copper and cupric ion; (*g*) silver ion and zinc. State in each case which elements are oxidized and which are reduced.

4. Complete the following incomplete equations:

(*a*) $H^+ + NO_3^- + Ag = Ag^+ + NO$;
(*b*) $H^+ + NO_3^- + Sn = H_2SnO_3 + N_2O_3$;
(*c*) $H^+ + NO_3^- + CuS = Cu^{++} + SO_4^{--} + NO$;

(*d*) $H^+ + NO_3^- + Zn = Zn^{++} + NH_4^+$;
(*e*) $Bi(OH)_3 + HSnO_2^- = Bi +$;
(*f*) $HAuCl_4 + Fe^{++} = Au +$;
(*g*) $P_4 + OH^- = PH_3 + H_2PO_2^-$;
(*h*) $As_2O_3 + H^+ + NO_3^- = H_3AsO_4 + N_2O_3$;
(*i*) $ClO^- + AsO_2^- = AsO_3^{---} +$.

5. What is meant by "noble" metals and "base" metals?

6. From the metals given in the table on page 234, construct the battery that would give the greatest electromotive force.

7. Explain how contact with zinc protects iron from corrosion.

8. How can you tell when a metal will dissolve in any of the following reagents: water, hydrochloric acid, nitric acid, sulfuric acid, sodium hydroxide?

9. How is the oxidizing power of H^+ affected by its concentration?

10. Explain the cleaning of silver by zinc or by aluminum.

11. How would you prepare each of the following:

(*a*) Br^- from Br_2;
(*b*) HCl gas from Cl_2;
(*c*) I_2 from NaI;
(*d*) $PbCrO_4$ from Pb and $CrCl_3$;
(*e*) Fe from $FeCl_3$;
(*f*) $Fe(OH)_2$ from Fe;
(*g*) Fe_2O_3 from $FeSO_4$;
(*h*) $Mn(OH)_2$ from MnO_4^-;
(*i*) HgCl from $HgCl_2$;
(*j*) Hg from $HgCl_2$?

12. How many grams of hydrogen peroxide are necessary to reduce 10 g. of $MnO(OH)_2$ to Mn^{++} in acid solution? *Ans.* 3.24 g.

13. A solution of $KMnO_4$ is standardized by titrating a ferrous solution made by dissolving 1.12 g. of pure iron. The volume of $KMnO_4$ solution required is 42.0 cc. The same permanganate solution is then used to determine the strength of a solution of hydrogen peroxide, 50 g. of the latter requiring 34.0 cc. of the former. What per cent of hydrogen peroxide is in the solution? (In this reaction Mn^{++} and O_2 are produced.) *Ans.* 0.55 per cent.

14. Manganese in the form of manganous ion can be titrated with a solution of potassium permanganate, MnO_2 being formed. Write the equation.

15. How many grams of $K_2Cr_2O_7$, in solution, would it take to oxidize the same amount of Fe^{++} as would be oxidized by 1.00 g. of $KMnO_4$, in acid solution?

16. Starting with metallic tin, how would you prepare in succession: $SnCl_2$, $SnCl_4$, SnO_2, SnO, SnS, SnS_2, $SnCl_4$?

17. How could you separate the metallic elements in a precipitate consisting of PbS, ZnS and SnS?

18. Why cannot HI be prepared by the action of concentrated H_2SO_4 on NaI?

CHAPTER XVI

PERIODIC SYSTEM

It became evident to chemists a long time ago that there are certain elements which may be grouped together by reason of their similarity. Among such groups may be mentioned lithium, sodium and potassium, commonly called the alkali metals; calcium, strontium and barium, the alkaline earth metals; fluorine, chlorine, bromine and iodine, called the halogens. In 1866 Newlands read a paper before the London Chemical Society in which he showed that if the then known elements were arranged in the order of increasing atomic weight, as follows:

H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca
1	7	9	11	12	14	16	19	23	24	27	28	31	32	35.5	39	40

there is a similarity between every eighth element in the series, so that if it is divided into groups of eight and these placed under each other in successive rows, as follows,

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	etc.			

then the elements standing in the same vertical column are those which correspond to each other in chemical nature. It is evident from the table that this is the case. Strange as it may seem this discovery was received with some ridicule, and its value not appreciated till later. In 1869 this same idea was more fully elaborated independently by Mendeléeff

and Lothar Meyer. Each of these chemists tabulated the elements substantially by the method shown in Table I, p. 254.

The fundamental idea expressed by such an arrangement is that of the periodic recurrence of properties as the atomic weights increase. This periodicity is shown graphically in

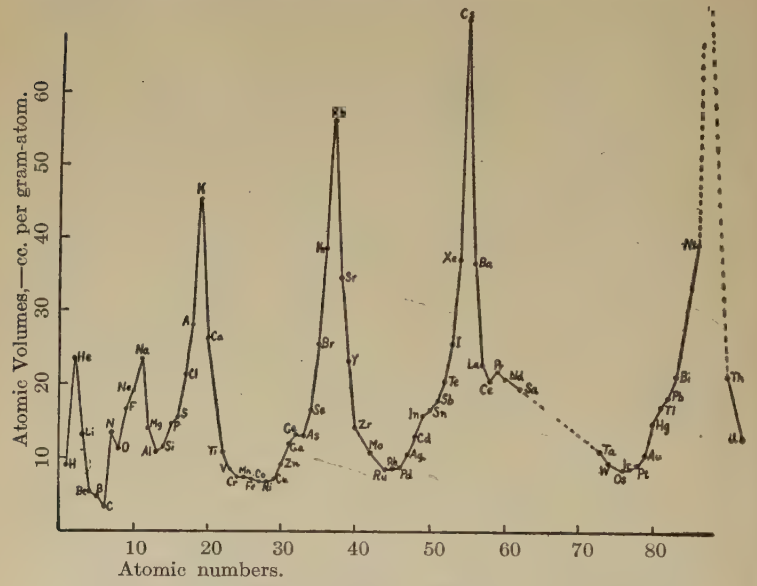


FIG. 12. — Periodicity of Atomic Volumes of the Elements.

Fig. 12, where atomic volumes (the number of cubic centimeters occupied by a gram-atom of the element) are plotted, not against atomic weights, however, but against the atomic numbers. The atomic numbers are whole numbers, roughly half the atomic weights, which have been determined by X-ray spectra, and which are more fundamental than atomic weights. It will be noticed that at the successive peaks are found similar elements, those of the alkali metals. The next

element to the left of each peak is a member of the group of rare inert gases, the next element to the right of each peak is an alkaline earth metal, and so on. The curve is thus made up of a series of roughly similar sections each of which

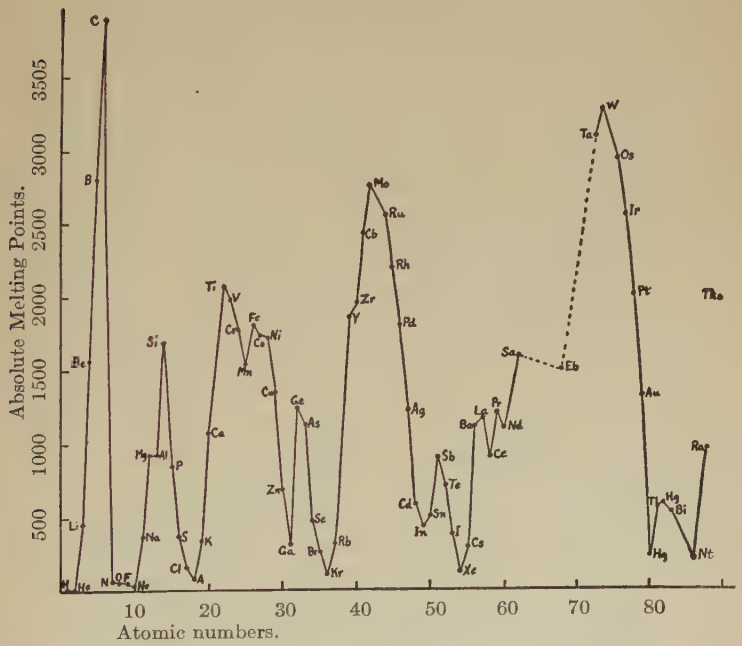


FIG. 13. — Periodicity of Absolute Melting Points of the Elements.

corresponds to a row of elements in the table. If the absolute melting points are plotted against the atomic numbers, we obtain the curve shown in Fig. 13, in which we see a similar periodicity. Here the troughs are occupied by the elements of the group of inert gases. This curve, likewise, could be cut up into a number of similar sections.

TABLE I

PERIODIC SYSTEM. — MENDELÉEFF (MODIFIED)

0	1	1′	2	2′	3	3′	4	4′	5′	5	6′	6	7′	7	8	9	10
	H																
	1																
He	Li		Be		B		C		N		O		F				
2	3		4		5		6		7		8		9				
Ne	Na		Mg		Al		Si		P		S		Cl				
10	11		12		13		14		15		16		17				
A	K		Ca		Sc		Ti		V		Cr		Mn		Fe	Co	Ni
18	19		20		21		22		23		24		25		26	27	28
		Cu		Zn		Ga		Ge		As		Se		Br			
		29		30		31		32		33		34		35			
Kr	Rb		Sr		Y		Zr		Cb		Mo		—		Ru	Rh	Pd
36	37		38		39		40		41		42		43		44	45	46
		Ag		Cd		In		Sn		Sb		Te		I			
		47		48		49		50		51		52		53			
Xe	Cs		Ba		La		Ce		(Rare earths, 59–72, unclassified.)								
54	55		56		57		58										
									Ta		W		—		Os	Ir	Pt
									73		74		75		76	77	78
		Au		Hg		Tl		Pb		Bi		Po		—			
		79		80		81		82		83		84		85			
Nt	—		Ra		Ac		Th		UX_2		U						
86	87		88		89		90		91		92						

Not only do the measurable physical properties, but also the chemical characteristics show a similar periodicity. If we used figures expressing the acidic or basic characteristics of the hydroxides of the elements, we would find a similar periodic curve.

The periodic classification of the elements is exceedingly useful in correlating a vast number of facts regarding the elements and their compounds so that they may be more easily remembered and also predicted. However, before discussing specific properties it will be well to consider certain defects in the Mendeléeff table, and other ways of representing the actual periodic behavior. In the first place, the Mendeléeff table throws into the same group such dissimilar elements as sodium and copper. In the second group zinc, cadmium and mercury show a little more resemblance to the main members of the group, though it is by no means striking. In each group there is a branching, after the second period, into a main group, whose elements resemble closely the first two elements of the group, and a sub-group, whose resemblance to the first two elements is less marked. This is shown in the table by setting the sub-groups to one side. As we go towards the middle of the table we find the sub-groups resembling the main group more and more closely, until we find, in the fourth group, that the two branches bear about equal resemblance to the first two elements. It is rather useful, for example, to have vanadium placed in the same group as phosphorus, less so to have chromium classed with sulfur, and of very little use to have manganese classed with chlorine. The placing of the sub-groups more and more to one side as the ends of the table are approached is an attempt to avoid this defect in the table by representing

this growing dissimilarity, and is very significant in the discussion of properties to be taken up later.

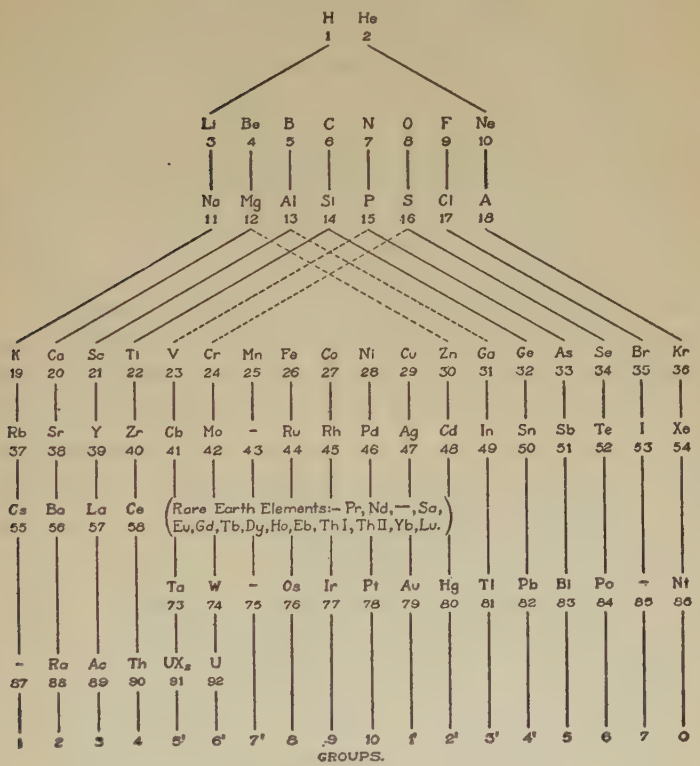
Again, Mendeléeff placed iron, cobalt and nickel and the platinum metals in the same group, regarding them as triplets really belonging in the same space on account of their nearly equal atomic weights. When the atomic numbers are used instead of atomic weights it is found that these are not triplets at all, and really belong in separate groups, as we have here indicated, by numbering them 8, 9 and 10, instead of including all these elements in group 8 as Mendeléeff did.

When atomic weights are used as the basis for the table there appears an anomaly due to the fact that the atomic weight of potassium is less than that of argon, though the latter should evidently come first. The same is true of tellurium and iodine, cobalt and nickel. The use of the atomic numbers, however, places all of these in their proper order.

Another arrangement of the Periodic System is indicated by the curves of properties, such as given in Figs. 12 and 13, and regards the elements of the sub-group as a new series intruding after the second period. This arrangement, first given by the Danish chemist Thomsen, is shown in Table II, and though it is not quite so easily remembered, it has advantages over the first form. It does not imply relationships between the sub-groups and the main groups which are slight or non-existent, and it places together such similar elements as nickel and copper, platinum and gold, etc. The slight relationships overemphasized by the Mendeléeff table between the main and sub-groups are here indicated by dotted lines.

TABLE II

PERIODIC SYSTEM. — THOMSEN


H He
1 2
Li Be B C N O F Ne
3 4 5 6 7 8 9 10
Na Mg Al Si P S Cl A
11 12 13 14 15 16 17 18
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36
Rb Sr Y Zr Cb Mo - Ru Rh Pd Ag Cd In Sn Sb Te I Xe
37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54
Cs Ba La Ce
55 56 57 58
(Rare Earth Elements:- Pr, Nd, —, Sa, Eu, Gd, Tb, Dy, Ho, Eb, Th I, Th II, Yb, Lu.)
Ta W - Os Ir Pt Au Hg Tl Pb Bi Po - Nt
73 74 75 76 77 78 79 80 81 82 83 84 85 86
- Ra Ac Th UX2 U
87 88 89 90 91 92
1 2 3 4 5' 6' 7' 8 9 10 1' 2' 3' 4' 5 6 7 0
GROUPS.

If three dimensions are used instead of two, it is possible to give a much more adequate representation of the periodic relationships. The Mendeléeff table would then be represented by a spiral on which the homologous elements fall below one another. The Thomsen table would then show the interpolated groups as branching off from the main spiral,

as shown in Table III, which is drawn according to an idea put forth by Soddy. This shows very clearly the nearly equal relationship of the two branches of Group 4 to carbon and silicon; the greater removal of Sub-Groups 3′ and 5′ from their main Groups, 3 and 5 respectively; the still greater divergence of Sub-Groups 2′ and 6′ from the corresponding main Groups; and the almost entire lack of relationship of Groups 1′ and 7′ with 1 and 7 respectively. On the other hand it brings out the fact shown by all curves of properties, *i.e.*, that the properties of the elements in the neighborhood of iron and platinum are farthest removed from those of the inert gases in Group 0. The peak represented by Group 0 is intended to indicate the abrupt change between Group 7 and Group 1.

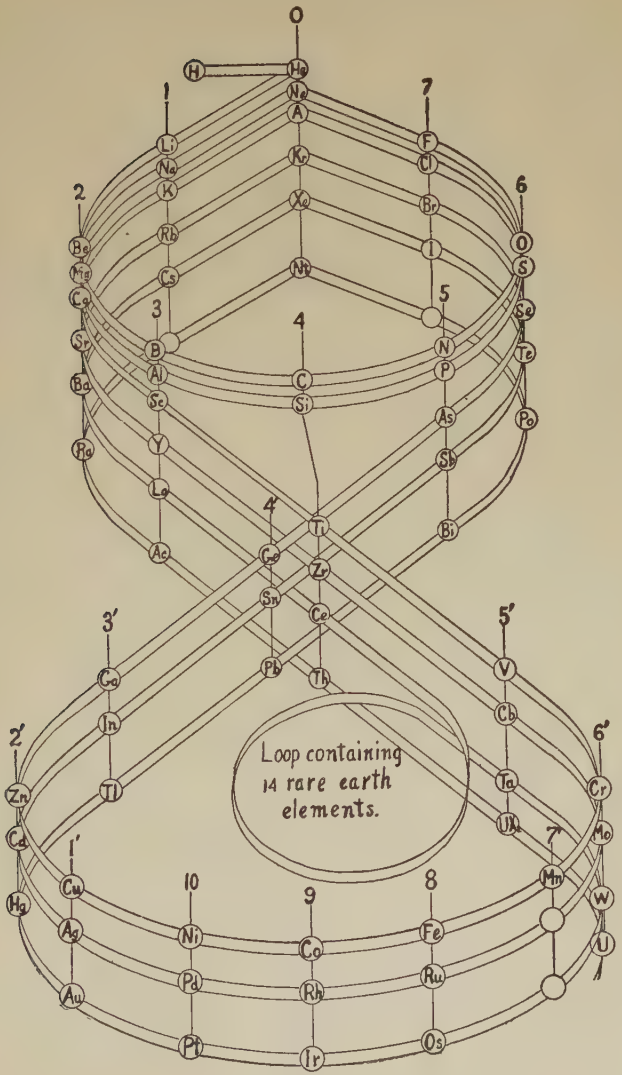
After becoming familiar with the basis of the Periodic System the student should familiarize himself with the position of the commoner elements in some one of the three forms of the system that have been given. The designation of the groups and sub-groups has been made the same in all of the forms, so that the following discussion will be equally intelligible whichever form of the table the student decides to adopt. It is far more important to become thoroughly familiar with one of the forms than it is to attempt to learn two or three of them with possible confusion.

We will now proceed to a discussion of the relationship between the position of an element in the table and its behavior.

Density. We have seen that as we go from one period to the next, *i.e.*, from top to bottom of each group, there is nearly always a small increase in the atomic volume, and that the elements with largest atomic volume are in Group

TABLE III

PERIODIC SYSTEM. — SODDY



1, and those of smallest atomic volume are among the iron and platinum metals. This corresponds to the fact that in general the elements increase in density as we go from the top to the bottom of each group, and that the heaviest elements are among the platinum metals, as illustrated by the following values:

DENSITIES OF SOLID ELEMENTS

Group 1	Group 2	Group 2′	Group 1′	Group 8	Group 10
Li 0.53	Be 1.73	Zn 7.1	Cu 8.9	Fe 7.9	Ni 8.7
Na 0.99	Mg 1.74	Cd 8.6	Ag 10.5	Ru 12.0	Pd 11.5
K 0.86	Ca 1.53	Hg 13.5	Au 19.2	Os 22.5	Pt 21.4
Rb 1.52	Sr 2.55				
Cs 1.90	Ba 3.78				

Melting Point. As shown by the curve in Fig. 13, the elements with the lowest melting point are in Group 0. The adjacent groups, 1 and 7, contain elements of low melting points, increasing as we approach Group 4, where we find carbon at the top with the highest of all melting points. Another maximum is found with tungsten, whose neighbors also have high melting points. Among the metals of the main groups the melting points decrease as we descend the group. The following values may serve as illustrations:

MELTING POINTS, ABSOLUTE

Group 1	Group 2	Group 2′	Group 1′	Group 8	Group 10
Li 459°	Be 1573°	Zn 692°	Cu 1356°	Fe 1800°	Ni 1725°
Na 371	Mg 924	Cd 594	Ag 1234	Ru 2570	Pd 1820
K 335	Ca 1083	Hg 234	Au 1336	Os 2970	Pt 2028
Rb 311	Ba 1123				
Cs 299					

Tensile Strength. The metals with the greatest tensile strength are found among the sub-groups, starting with 5 and extending to 10. These groups include iron and the

metals alloyed with it to make the modern alloy steels of such remarkable properties, V, Cr, Mo, W, U, Mn and Ni.

Valence. Very striking relationships are found for the valence of the elements in the main groups. The inert gases are commonly said to have zero valence, corresponding to their group number. The alkali metals in Group 1 have a valence in their compounds of + 1, the alkaline earth metals a valence of + 2, and the valence of the elements in each succeeding group increases with the group numbers, as illustrated by the formulas of the oxides and chlorides.

Li_2O	BeO	B_2O_3	CO_2	N_2O_5	——	——
$LiCl$	$BeCl_2$	BCl_3	CCl_4	——	——	——
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	——	——

With the fourth group and those following lower valences also appear, as in CO, P_2O_3, SO_2, etc., and a negative valence becomes evident, as shown in their compounds with hydrogen.

CH_4	NH_3	H_2O	HF
	PH_3	H_2S	HCl
	AsH_3	H_2Se	HBr

The limiting values of the valences in the main groups seem, therefore, to be as follows:

Group	0	1	2	3	4	5	6	7
Valence	0	+ 1	+ 2	+ 3	+ 4 − 4	+ 5 − 3	+ 6 − 2	+ 7 − 1

Other valences lying between these extreme values may be found, as shown by the following:

	Valence of P		Valence of Cl
P_2O_5	+5	$KClO_4$	+7
P_2O_3	+3	$KClO_3$	+5
H_3PO_2	+1	$KClO_2$	+3
H_3P	−3	KClO	+1
		KCl	−1

In the sub-groups valences corresponding to the group number usually appear, but they are not always the most characteristic, and other valences appear which might not be expected on the basis of the Periodic System. The following table illustrates this fact:

	Valences
Cr	2, 3, 6
Fe	2, 3
Mn	2, 3, 4, 6, 7
Pt	2, 4
Os	2, 4, 8

The horizontal relationships are rather more important than the vertical relationships with these elements, as illustrated by the fact that the valence + 2 is characteristic of the successive elements, Cr, Mn, Fe, Co, Ni, Cu, Zn. Again Cu and Ni are more alike than Ni and Pd, or Cu and Ag, and Au is rather more like Pt than Ag.

It is rather striking that the rare earth elements, which seem to be out of harmony with the rest of the system, all have + 3 as their most characteristic valence.

Noble and Base Metals. In the main groups there are no noble metals; all of the metals in these groups are easily oxidized. The noble metals are found rather in the sub-groups, and at the bottom. Thus in Group 2′ we have first

zinc, a base metal, cadmium, a less base one, and finally mercury, a rather noble metal. In Group 1′ we have copper, intermediate between the two classes, then silver, about as noble as mercury, and finally gold, one of the noblest of all. At the bottom of the adjacent Groups 10 and 9 we find respectively platinum and iridium, metals which are exceedingly difficult to attack.

Metals and Non-metals. It has been pointed out in Chapter V that the distinction between metals and non-metals is of fundamental importance in connection with the chemical behavior of the elements. We have seen, further, that this distinction may be expressed by saying that the more metallic an element is the more prone it is to take on a positive valence, and the more non-metallic it is the more prone it is to take on a negative valence. Or, we may say more briefly, the more metallic elements are more electropositive, and the less metallic elements are more electronegative.

It must be noted that this distinction is different from that between noble and base metals. A highly metallic element is one which is a good conductor of heat and electricity, has a high reflective power for light, is ductile and malleable, and tends to form compounds in which it is the positive element. According to these criteria, sodium, which is so base that it rapidly oxidizes in the air and decomposes water vigorously, is a more metallic element than the much nobler metal, tin.

The most electropositive elements are in Group 1, and the most electropositive of these is cæsium, at the bottom. In all of the main groups the most metallic or electropositive element is at the bottom. The metallic character decreases as we go from group to group, until, in Group 7, we find

elements which are all highly electronegative. In Group 6 we have the non-metallic elements, oxygen and sulfur, at the top, but the weakly metallic tellurium at the bottom. In Group 5 we find nitrogen at the top entirely non-metallic in character, phosphorus non metallic but with a weakly metallic allotropic form, arsenic with metallic luster but brittle and volatile, antimony a fairly good metal, and bismuth at the bottom quite metallic in nature, forming no compounds in which it shows a negative valence as do the others (*e.g.*, AsH_3). In Group 4 we find at the top the non-metal carbon with an allotropic modification, graphite, in which it shows faint metallic properties. As we approach the bottom the metallic character quickly predominates, as in tin and lead.

This change in metallic character from group to group and from top to bottom of each group serves to correlate a vast array of facts which we have space only to illustrate.

Strength of Acids and Bases. One of the most important chemical characteristics of the metals is that their hydroxides are bases, as discussed in Chapter V. Since we have elements of all degrees of electropositive character we have bases of all degrees of strength. The strongly positive alkali metals give hydroxides which are powerful bases, and the strongest of these is, as we should expect, cæsium hydroxide. The hydroxides of the metals of Group 2 are weaker, that of beryllium, at the top, being a rather weak base, though the strength increases as we descend the group, until, in barium hydroxide, we have a base approaching those of Group 1 in strength.

When a base is sufficiently weak it may often show the complementary behavior of an acid, and in the presence of

very concentrated alkali beryllium hydroxide will dissolve, so that we may regard it as an extremely weak acid. In Group 3 this acid character becomes more pronounced, and $B(OH)_3$ (or H_3BO_3) is a strong enough acid to turn blue litmus paper red. The basic character, however, is practically absent. There exists, it is true, BCl_3, which may be regarded as the salt of $B(OH)_3$ with HCl, but it is completely hydrolyzed by water, and hence cannot be formed in aqueous solution. $Al(OH)_3$ is, as we should expect, a much weaker acid, and is, at the same time, a weak base.

The corresponding compounds with carbon and silicon, H_2CO_3 and H_2SiO_3 (or $SiO(OH)_2$ or $Si(OH)_4$, etc.), are weak acids, H_2TiO_3 is amphoteric, *i.e.*, both acidic and basic, whereas $Th(OH)_4$ is a base only. The hydroxides of tin and lead are amphoteric, with the basic character most marked in the latter. As a consequence salts of Sn^{++} are more hydrolyzed than those of Pb^{++}.

Comparing similar compounds in Group 5 we find that HNO_3 is a strong acid, HPO_3 (or H_3PO_4) is a moderately strong acid, H_3AsO_4 is a weak acid, H_3SbO_4 is a very weak acid and a very weak base. With the corresponding trivalent compounds we go from the moderately weak acid HNO_2 to the weak base $Bi(OH)_3$ exactly as we should expect.

It may aid somewhat in understanding this connection between metallic character and the behavior of the hydroxide to compare such compounds as KOH, potassium hydroxide, and ClOH (or HClO), hypochlorous acid. In these compounds the potassium and chlorine are both positive, but the latter can be only weakly positive since its normal tendency is to become highly negative, as in HCl and KCl. If we attempt to represent the relative positive and negative

characters of the elements involved by the size of the charges we write under them, we will get some such results as the following:

Now when dissociation takes place it tends to break up a compound into parts having charges of as nearly equal intensity as possible; accordingly, there is a weak tendency for ClOH to ionize into ClO^- and H^+, which makes it a weak acid, whereas KOH ionizes strongly into K^+ and OH^-, making it a strong base. In a compound like AlO(OH), aluminum hydroxide, where the aluminum and the hydrogen have about the same "positivity," OH^- or H^+ may split off with nearly equal readiness, so that the substance is amphoteric.

Amphoteric Sulfides. The relationships involving the solubility of sulfides pointed out in Chapter XII may also be correlated in accordance with the Periodic System. Thus, of the three sulfides, As_2S_3, Sb_2S_3 and Bi_2S_3, the first, the sulfide of a rather non-metallic element, is sufficiently acidic to dissolve easily in sulfide ion, S^{--}, forming AsS_2^-; the second, Sb_2S_3, dissolves with difficulty, while Bi_2S_3 is insoluble in this reagent.

Stability of Hydrides. In the hydrogen compounds of the elements in Groups 5, 6 and 7, the hydrogen is doubt-

less always the positive element, and therefore the more electronegative the other element the more stable is the compound. Nitrogen, for example, is non-metallic and assumes the negative valence rather easily; hence ammonia, NH_3, is a moderately stable compound which will withstand moderate heating without decomposing. As we descend the group we find that PH_3, AsH and SbH_3 become increasingly easy to decompose by heating, while the last element of the group, bismuth, is so metallic that it will not assume the negative valence at all, hence gives no compound with hydrogen.

Oxygen, the first member of Group 6, is far more electronegative than nitrogen, and therefore gives a much more stable hydride, water, which will break down into its elements only at extremely high temperatures, being only about 2 per cent dissociated at 2000° C. Hydrogen sulfide is considerably less stable, and hydrogen telluride, finally, decomposes spontaneously, and is prepared with difficulty.

A similar decrease in stability is found in Group 7 as we descend from the very stable hydrogen fluoride and hydrogen chloride to the rather easily decomposable hydrogen iodide.

Comparison of Oxides and Halides of Other Positive Elements. The relationships with compounds of the metals with the members of Groups 5, 6 and 7 are parallel to those already noted with the hydrides. For example, cupric iodide does not exist, while cupric chloride and bromide do. Copper is not sufficiently electropositive and iodine sufficiently electronegative for this compound to be stable, consequently the attempt to prepare it results instead in the formation of cuprous iodide and iodine.

$$Cu^{++} + 2\,I^- = CuI + \tfrac{1}{2}\,I_2.$$

Molybdenum trioxide exists, MoO_3, but chlorine, which is less electronegative than oxygen, cannot call forth the highest valence of molybdenum, which forms only a pentachloride, $MoCl_5$. With fluorine, however, which is the most electronegative of all the elements, the molybdenum can again be hexavalent, and we have the hexafluoride, MoF_6.

If we compare the compounds of sulfur with bromine, chlorine, oxygen and fluorine, which is the order corresponding to increasing electronegative character, we find that the highest bromide has the formula S_2Br_2; a chloride exists, SCl_4, in which the sulfur has a higher valence; in sulfur trioxide, SO_3, sulfur has its maximum positive valence, but the compound breaks down rather completely above 700° C. into SO_2 and O_2; and finally the fluoride, SF_6, is an exceedingly stable inert substance. Illustrations of this sort might be multiplied almost indefinitely.

Solubility of Salts. The solubility of salts changes in regular order according to the Periodic System in nearly all instances. This may be illustrated for a single group, the second, by the following table:

	Hydroxide	Sulfate	Chloride
Magnesium	Insoluble	Soluble	Deliquescent
Calcium	Sparingly soluble	Sparingly soluble	Deliquescent
Strontium	Moderately soluble	Insoluble	Soluble
Barium	Soluble	Very insoluble	Less soluble

It may be mentioned that a similar order is shown by the more soluble salts of the alkali metals, where, for example,

the least soluble sulfate is that of cæsium, at the bottom of the group.

Elements That Form Complex Ions. The elements most prone to form complex ions are in the sub-groups and especially in the neighborhood of Group 1′ in the second and third forms of the table. Complex ions with ammonia are given by Zn, Cd, Cu, Ag, Ni and Co. Complex cyanides are given by the same elements, also by the platinum metals and iron. Complex chlorides are given chiefly by the platinum metals and gold, as illustrated by $PtCl_6^{--}$ and $AuCl_4^{-}$.

Resemblance between the First Member of a Group and the Second Member of the Succeeding Group. There appears a striking similarity between the first element in Groups 1 and 3 and the second element in the succeeding group. Thus lithium, though an alkali metal, resembles magnesium in having a hydroxide and carbonate which are not very soluble, a rather insoluble phosphate and a deliquescent chloride. Beryllium is so much like aluminum that the two elements are difficult to separate. Boron is like silicon in physical properties and gives compounds similar in many respects. The borates of all but the alkali metals, like the corresponding silicates, are insoluble in water, and when fused tend to give glasses on cooling.

Radioactive Elements. As might be expected, it is the heaviest and most complex atoms which tend to break down into simpler ones, and all of the elements of higher atomic weight than bismuth are radioactive. These are, accordingly, found at the bottom of the table.

Prediction of Unknown Elements. The value of the Periodic System was demonstrated in very striking fashion by the prediction of unknown elements by Mendeléeff. At

the time he constructed his table it was obvious that several gaps should be left in order to have the succeeding elements fall into their proper groups. Such gaps were to be found at the places now filled by scandium, gallium and germanium. From the properties of the adjacent elements, Mendeléeff predicted the properties of the unknown elements. The remarkable accuracy of these predictions is illustrated by the following comparison of the unknown element called by Mendeléeff "ekasilicon," with germanium, discovered later by Winkler.

Ekasilicon	Germanium
At. wt. 72, density 5.5.	At. wt. 72.5, density 5.46.
Oxide EsO_2, density 4.7.	Oxide GeO_2, density 4.7.
Chloride $EsCl_4$, liquid, boiling slightly below 100°, density 1.9.	Chloride, $GeCl_4$, liquid, boiling at 86°, density 1.887.
Ethide, $Es(C_2H_5)_4$, liquid, boiling at 160°, density 0.96.	Ethide, $Ge(C_2H_5)_4$, liquid, boiling at 160°, density slightly less than 1.
Fluoride, EsF_4, not gaseous.	Fluoride, GeF_4, white, solid.

The foregoing comparison should serve as an illustration of the value of the Periodic System to the student of chemistry, for if an undiscovered element can be foretold so brilliantly by its aid, then any knowledge a student may have of some elements may be similarly projected to deduce the properties of adjacent elements. The use of the Periodic System, therefore, enormously increases the effectiveness of a given amount of mental effort, and it is very important to form the habit of using it constantly.

CHAPTER XVII

THE CONSTITUTION OF THE ATOM

For a long time scientists have considered the possibility that the chemical elements may not be ultimate forms of matter, and that just as the vast number of known substances are composed of a relatively small number of elements, so these elements themselves may, in turn, be composed of one or more still more fundamental forms of matter. Plausibility was lent to this assumption by the fact that the atomic weights of the lighter elements approximate whole numbers to a degree utterly improbable from the standpoint of the laws of chance. It seemed, therefore, as urged first by Prout, that hydrogen, with an atomic weight close to 1, might be the fundamental element from which the others are constructed. However, as atomic weights were more accurately determined, it was found that the deviations from whole numbers are too large to be attributed to experimental error, especially in the case of chlorine, with an atomic weight of 35.5. This made Prout's hypothesis inconsistent with the law of conservation of mass, and therefore it could not be accepted literally, although it was still recognized that it must represent an approach to the truth, and that there must be something common to the elements in order to produce such an approach to whole numbers in their atomic weights.

The fact that the elements lend themselves to the arrangement into groups of related elements as shown in the Periodic System points almost irresistibly to the existence of some unit or units common to the atoms of different elements, and arranged similarly in all of the elements in any one group. It still remained, however, to discover the smaller units of matter out of which the atoms are constructed. Light was thrown upon this question, first, by a study of the phenomena accompanying the electric discharge in an evacuated tube, and second by the discovery of radium and the other radioactive elements. We will take up these two sets of phenomena in order.

Cathode Rays. When an electric discharge is sent through a highly evacuated tube provided with sealed-in electrodes, there is given off from the cathode a characteristic discharge called **cathode rays**. Unlike light, these rays are almost entirely stopped by the glass walls of the tube, producing a fluorescence upon the glass where they strike. A screen of fluorescent material like zinc sulfide, if put into the tube in the path of the rays, shows a brilliant fluorescence, very useful in studying these rays. They are deflected from a straight path by either a magnetic or an electric field, in such a way as to indicate that they consist of streams of negatively charged particles, moving with great velocity, which have been called **electrons**.

By measuring the extent of this deflection by both kinds of field, it has been possible to calculate the ratio of the charge on each electron to its mass, and also the speed of the electrons. It is evident that some such calculation should be possible, because any moving body can be deflected from a straight line by a known force to an extent dependent

upon its mass and its speed. It obviously takes more force to deflect a swiftly moving bullet than a slowly moving golf ball, and still more force to deflect the heavy shell of a big gun.

The result of these measurements and calculations, carried out by J. J. Thomson, shows that the speed of the electrons ranges from 10,000 to 100,000 miles per second, a speed approaching that of light, which is approximately 200,000 miles per second. The ratio of the charge to the mass of the electrons is found to be 1845 times the corresponding ratio for a hydrogen ion, which is 96,500 coulombs per gram. Therefore, either the mass of the electrons is less, or the charge is greater than that of a hydrogen ion. Now it has been found that the charge is the same (though opposite in sign), hence we are led to the conclusion that the mass of the electron is $\frac{1}{1845}$ of that of the hydrogen ion, the smallest particle of matter previously known.

The discovery of the electron provided the unit out of which atoms may be considered as being constructed, and the fact that the nature of the electrons' composition, the cathode stream, is entirely independent of the nature of the cathode used as well as of the residual gas in the tube, indicated that atoms of all substances contained the same kind of electrons.

X-rays. When the electrons of the cathode stream are suddenly stopped by hitting a target within the evacuated tube, a different sort of rays is given off from the target. These are called Roentgen Rays, after their discoverer, or X-rays, in allusion to their formerly mysterious character. Unlike the cathode rays, they penetrate not only the glass walls of the tube with ease, but many substances quite opaque

to ordinary life, such as paper, leather, flesh or wood. Metallic substances are more or less opaque to them.

The behavior of the X-rays shows them to be quite different from any streams of particles, such as the cathode rays. The fact that they cannot be reflected or refracted like ordinary light proved very difficult to explain until it was shown that this behavior is due to their extremely short wave length, about 0.001 that of ordinary light. It is now known that owing to this short wave length no obtainable surface is smooth enough to reflect or refract them. Their wave length is of the same order of magnitude as the distances between the atoms in the face of a crystal. These regularly placed atoms in a crystal face may, however, act as a diffraction grating to the X-rays, just as closely ruled lines upon a glass surface give a diffraction grating for ordinary light, and knowing, as we do, the distances between the atoms on a crystal face, we can calculate the wave length of X-rays, just as we calculate the wave length of ordinary light by the aid of a diffraction grating.

We have concluded, therefore, that the X-rays are like ordinary light in that they are electromagnetic waves, and unlike it merely on account of their vastly smaller wave length. Just as some substances are opaque, for example, to blue light but transparent to red light, so many substances opaque to ordinary light are transparent to X-rays. It is this property of penetrating many substances opaque to ordinary light that makes the X-rays of such great value in surgery. By their use it is possible to make visible the bones of the body and to detect the position in the body of foreign metallic objects, such as bullets.

The eye is not sensitive to X-rays, so that it is necessary,

in order to detect them, to use a photographic plate, which is sensitive to them, or else a fluorescent screen of certain substances like zinc sulfide or barium platinic cyanide.

Another important effect of the X-rays is their ability to ionize gases, *i.e.*, to make a gas conduct by producing charged molecules capable of wandering in an electric field, and hence of carrying current.

It is worth noting that the discovery of the X-rays was the result of pure scientific research, and not the effort of one endeavoring to discover something of immediate practical value. It is such work which produces the most practical results in the long run. No one would set out to discover X-rays for the sake of gaining riches, for few who undertake such work ever do. Their discovery, however, furnishes a brilliant example of the material as well as the moral value to mankind of the search for truth, and emphasizes the hearty support which society should give to all research in pure science.

Canal Rays. In addition to the negative electrons produced by an electric discharge in an evacuated tube, there occur rays, called **canal rays**, composed of positive particles. By suitable construction of the apparatus it is possible to separate these particles from the negative electrons and to measure their charge and mass, just as is done with the latter, by means of the deflection produced by magnetic and electric fields. Such experiments show that unlike the negative electrons, both the charge and the mass of these particles depend upon the nature of the gas left in small amount in the tube. The charge is some simple multiple of the elementary charge, and the mass is never less than that of the hydrogen atom, but is such as to indicate that

the particles are a mixture of the molecules of the gas put into the tube together with the smaller atoms or molecules resulting from their decomposition.

Radioactivity. The French physicist Becquerel discovered that certain substances, notably uranium compounds, give off a radiation capable of affecting a photographic plate through black paper and other substances opaque to ordinary light, and capable of ionizing gases, as shown by the fact that such substances hasten the discharge of an electroscope. This activity, known as radioactivity, is shown by uranium and thorium compounds to an extent dependent upon their content of uranium or thorium respectively. The activities of different materials can be easily compared by measuring the time required for the gold leaf of an electroscope to fall through a certain angle under otherwise identical conditions.

Madame Curie determined the activity of a number of uranium compounds and found that certain uranium-bearing minerals were more radioactive than their uranium content would indicate. With the coöperation of her husband she made a series of chemical separations, constantly saving the radioactive portion and rejecting the inactive portion, until she had isolated radium, a new element, with an atomic weight 226, chemically very similar to barium, but with a radioactivity several million times that of uranium.

The properties of radium proved to be so remarkable that many investigators turned their attention to it with results of the utmost importance for both chemistry and physics. It was found that the radiation consisted of three parts, first, β-rays, consisting of electrons, identical with those of the cathode stream in an X-ray tube, easily de-

flected by a magnet, of moderate penetration and ionizing power; second, γ-rays, identical with X-rays, except for their greater "hardness" or penetrating power; and third, α-rays, analogous to the canal rays, positively charged, much heavier than the negative electrons, so that they are but feebly deflected by a magnetic field. They are unable to penetrate very far through matter, being stopped by even a few centimeters of air. However, because they are stopped by gas molecules, they ionize the latter very highly, so that an electroscope is highly sensitive to them. They produce individual scintillations on a screen of zinc sulfide which have made it possible to count the number of α-particles given off from radium, showing that 1.36×10^{11} particles are given off per second per gram of radium.

When radium salts are heated, or when they are dissolved in water, it is possible to obtain a minute quantity of a highly radioactive gas called **radium emanation**, leaving the radium temporarily inactive. This gas behaves like a member of the O group of chemical elements, analogous to helium, argon, etc. Its molecular weight has been calculated from its speed of diffusion to be 222. It has been given the name **niton**, and assigned a place in the Periodic System of elements. It loses one half of its radioactivity in 3.85 days, while the radium from which it was obtained recovers half of its maximum activity in the same period, showing that the emanation is being constantly produced from radium at a definite rate.

As the emanation decays, it produces the stable element helium, as shown conclusively by the appearance of the helium spectrum when an electric discharge is sent through a tube containing the gas. This remarkable observation was first made by Ramsay and Soddy, and has since been abun-

dantly confirmed by others. The alchemists of the Middle Ages sought in vain to transmute the baser metals into gold, and their failures led chemists until recent times to regard the elements as more or less eternal and unchangeable. Now, however, the transmutation of elements has been actually observed, and though, to those seeking sudden riches, the production of helium is less alluring than the production of gold, the scientific importance of this new knowledge is none the less on that account.

It is now known that the α-particle shot off during many radioactive changes is simply a helium atom minus two electrons, so that when it is stopped, and succeeds in attaching two electrons, it becomes a helium atom.

It has been shown that there exist whole series of radioactive elements — definite chemical substances with places in the Periodic System — changing one into the other with velocities characteristic of each element and independent of external conditions. In the accompanying table are given the elements produced by the disintegration of uranium, together with their places in the Periodic System, their atomic weights, average life period and their characteristic radiations. There is another series in which uranium 1 changes through uranium Y to actinium and a further series of elements. Still another series starts with thorium and includes 12 disintegration products.

The discovery of these radioactive changes has made it necessary to distinguish them from chemical reactions, which likewise give rise to new substances, and to define an element in such a way as to distinguish between radioactive disintegration of elements and the decomposition of chemical compounds (cf. Chapter I).

THE URANIUM-RADIUM SERIES OF RADIOACTIVE ELEMENTS

ELEMENT	AVERAGE LIFE	ATOMIC WEIGHT	GROUP IN PERIODIC SYSTEM	KIND OF RAYS*
Uranium 1	8×10^9 yr.	238	6′	α
Uranium X_1	35.5 da.	234	4	β
Uranium X_2	1.65 min.	234	5′	β
Uranium 2	3×10^6 yr. (?)	234	6′	α
Ionium	2×10^5 yr. (?)	230	4	α
Radium	2440 yr.	226	2	α
Niton	5.55 da.	222	0	α
Radium A	4.3 min.	218	6	α
Radium B	38.5 min.	214	4′	β
Radium C	28.1 min.	214	5	β
Radium C′	10^{-6} sec. (?)	214	6	α
Radium D	24 yr. (?)	210	4′	β
Radium E	7.20 da.	210	5	β
Radium F (Polonium)	196 da.	210	6	α
Lead		206	4	
Radium C also changes to a small extent into Radium C_2	1.9 min.	210	3′	β
End. Lead (?)		210	4′	

The essential difference between a radioactive change and an ordinary chemical reaction seems to be that the former cannot be controlled by external conditions, such as changes of pressure or temperature, while the latter can. Both changes give rise to new substances, but whereas a chemical compound, on the one hand, may be decomposed at will by proper control of environment into its constituent elements, an element, on the other hand, if it changes at all into one or more other elements, does so at a rate absolutely beyond control.

* The β-rays are nearly always accompanied by γ-rays.

We may note also that the quantities of energy involved in the two types of change are of a different order of magnitude. A gram of radium, for example, gives off 132 calories of heat per hour throughout its average life of 2440 years. A gram of radium emanation in totally decomposing would give off 2.44×10^9 calories. On the other hand, the formation of one gram of water from oxygen and hydrogen, a chemical reaction which gives out an unusually great amount of heat, is accompanied by the liberation of 3800 calories, approximately one millionth of the heat liberated by the disintegration of the same weight of niton. If science should ever succeed in decomposing atoms at will, it staggers the imagination to think of the enormous quantities of energy that would be made available.

The Electrical Origin of the Mass of the Electron. It is found that the speed of the α- and β-particles shot off in radioactive changes depends upon the stability of the radioactive elements emitting them. Those elements which decompose rapidly emit their particles with greater velocity than do those of greater stability. This has made it possible to get electrons moving at widely different speeds, and has given rise to experimental results of a most amazing character.

On measuring the velocity and the ratio of the charge to the mass of the electrons, as was done for the cathode rays, it was found that their mass, as measured of course by their inertia, increases rapidly with their velocity as the latter approaches the velocity of light. This result had been predicted by the aid of electromagnetic theory. We know that an electric current possesses inertia, that is, it tends to keep on going, as shown by the sparking that occurs when a current is broken. This phenomenon is known as

self-induction. Now a charged particle, when moving rapidly, must behave like an electric current, so that it would have a greater inertia, and hence a greater mass, than it would have if uncharged or at rest. Now it is not possible to detect any additional inertia due to an electric charge on such a body as a pith ball, because we cannot make it move fast enough. But the electrons are shot off at such high speeds that the effect becomes very strongly marked. The astonishing thing is that the change in mass with velocity is exactly what we would expect if all of the mass of the electron were electrical. It is not necessary to assume two kinds of mass for the electron, one electrical in origin, the other non-electrical. We are therefore led to the conclusion that an electron is not a particle of matter plus an electric charge, but is simply an electric charge, an atom of electricity. And since, as we shall see, the atoms are made of electrons, it would appear probable that matter is composed solely of electricity.

The Constitution of the Atom. The disintegration of the elements which has been shown to accompany radioactive changes makes it evident that some elements change into others by reason of a change in the number and arrangement of the electrons constituting the atoms. We are led to believe that the atoms consist of negative electrons together with positive charges whose nature is more mysterious. These latter may be atoms of positive electricity, similar to the negative electrons, although they must be smaller, for their charge is more intense, as if concentrated into a smaller volume. It has not been possible to isolate the positive charge and study it as it has been possible to study the negative charge. Recent researches

indicate that the positive electricity in an atom is concentrated at the center, while the equivalent amount of negative electricity is present in the form of negative electrons. Some of these electrons are at distances from the positive nucleus which imply a structure for the atom analogous to that of the solar system. It is calculated that the negative electrons have a radius but one fifty-thousandth of that of the atom, whereas the radius of the positive nucleus is but one two-thousandth of that of the negative electron.

Light is thrown on the structure of the atom by some beautiful experiments carried out by C. T. R. Wilson. When air is supersaturated with water vapor the latter may not condense to mist unless suitable nuclei are present. Such nuclei can be furnished by gaseous ions, produced by the action of X-rays or by the α-, β- or γ-rays upon the gas. The path of an α- or β-particle may thus be made visible by photographing the train of mist it leaves in its wake when passing through air supersaturated with water vapor.

Since we know the diameter of the molecules of gas it is possible to calculate that the particles pass not between but right through thousands of molecules, which would only be possible if the molecules had the open structure mentioned above. The passage of an α- or β-particle through an atom is thus analogous to the passage of a comet through the solar system. The ionization of the gas is produced by the detachment of some of the outer electrons from the atom.

It has been observed that whereas the β-particle is frequently deviated from a straight line by passing near the electrons of the atoms through which it passes, the α-particle, which

is a helium atom thousands of times heavier than a β-particle, cannot be deflected by passing near the latter, but is only deflected when it happens to pass near the minute positive core of the atom, in which is concentrated nearly all of the atomic mass.

The Atomic Number. We have learned that when cathode rays impinge upon a target they give rise to X-rays. It has recently been possible to determine the wave length and vibration frequency of X-rays by using the face of a crystal as a diffraction grating Moseley, in a brilliant series of experiments, investigated the relation of this vibration frequency to the nature of the element constituting the target, and found that, with several exceptions, the square of the frequency increases by the same amount as we go from each element to that of next higher atomic weight. These exceptions, very strikingly, are those elements whose atomic weights obviously do not correspond to their proper place in the Periodic System, already discussed in a previous chapter (p. 255). Thus tellurium, with an atomic weight of 127.5, greater than that of iodine, which is 126.9, must nevertheless come in Group 6, before iodine, which is in Group 7. Now the X-ray spectra indicate this same order, making tellurium the fifty-second element and iodine the fifty-third. This atomic number, the number expressing the order of sequence of the elements as determined both by X-ray spectra and by chemical nature, is more fundamental than the atomic weight, and has been used in the forms of the periodic table given in the previous chapter.

A most interesting result is that below uranium the only gaps for missing elements are for the atomic numbers 43, 61, 72, 75, 85 and 87, indicating with much more certainty than

does any form of the periodic table that these are the only elements remaining to be discovered. There is every reason to believe that the last two would be radioactive and exceedingly unstable. Harkins has shown that the elements of even atomic numbers are relatively far more abundant.

It seems certain also that the atomic number is related to the number of positive charges in the nucleus of the atom, and that this nucleus consists of both positive charges and negative charges very closely packed, which are not disturbed by ordinary chemical reactions, but which are shot out as α- or β-particles respectively. The positive charges are probably in excess of the negative in the atomic nucleus, so that to have a neutral atom it is necessary for the compact nucleus to be surrounded by a number of negative electrons, which seem to be placed at relatively greater distances from the nucleus. It is these electrons which are knocked off when a gas is ionized, and which are chiefly responsible for the chemical properties of the atom.

It seems that an outer ring or group of eight electrons constitutes an especially stable arrangement so that atoms readily lose or gain electrons so as to make the number 8.

Electron Arrangement and Chemical Valence The facts of chemical valence seem to be connected with this outer group of electrons. For example, a hydrogen atom doubtless consists of the simplest possible nucleus, one positive charge, together with one negative electron. This electron may be taken up by some other atom, leaving hydrogen ion, H^+.

An atom of helium, or of the other elements in Group 0, holds the other electrons in such stable arrangement that these atoms display no chemical affinity.

An atom of one of the alkali metals consists of the nucleus of positive and negative electrons with an excess of one positive charge. This unit positive charge in excess in the nucleus is compensated by one outer negative electron, as with the hydrogen atom. This outer electron may be given up quite readily, which accounts for the fact that these metals have a valence of + 1.

The core of an atom in Group 2 contains two positive charges in excess, compensated by two negative electrons in the outer structure. The possible loss of these accounts for the valence of + 2 characteristic of the elements of this group.

The excess positive charge in the nucleus, and hence also the number of electrons in the outer ring, increases by one for each group of the Periodic System, so that for an element like phosphorus we have a net nuclear charge of + 5 surrounded by 5 negative electrons. Now there are two ways to get a more stable arrangement of outer electrons. One of these would be to add 3 more electrons, the other would be to remove 5 electrons. The first may be done by using three hydrogen atoms, whose three electrons fit into the missing places of the phosphorus atom. G. N. Lewis, who has carefully elaborated these ideas, represents the nucleus of the atom by its ordinary symbol, and the surrounding electrons by dots. Thus a hydrogen atom would be represented by the symbol · H, a sodium atom by · Na, a phosphorus atom by :Ṗ:, an oxygen atom by :Ö:, a chlorine atom by :C̈l:, etc. Now it is evident that three hydrogen atoms can combine with a phosphorus atom so that the three electrons of the former make up the stable group of 8 surrounding the latter, thus

$$\begin{matrix} & & \cdot\cdot & & \\ & & \mathrm{P} & & \\ & \cdot\cdot & : & \cdot\cdot & \\ \mathrm{H} & : & & : & \mathrm{H} \\ & & \mathrm{H} & & \end{matrix}$$

This would be a molecule of phosphine, PH_3.

Similarly, an oxygen atom needs the electrons of two hydrogen atoms, a chlorine atom needs that of one hydrogen atom to make up the stable group of 8. The formation of water and of hydrochloric acid respectively would thus be represented as follows:

$$\cdot\ddot{\mathrm{O}}\cdot + 2\,\mathrm{H}\cdot = \mathrm{H}:\ddot{\mathrm{O}}:\mathrm{H}$$

$$\cdot\ddot{\mathrm{Cl}}: + \mathrm{H}\cdot \quad = \mathrm{H}:\ddot{\mathrm{Cl}}:$$

When some force tends to pull these atoms apart, the tendency to retain the group of 8 electrons may be so great as to cause the hydrogen to be pulled off minus its electron, as hydrogen ion, while the chlorine atom with its extra electron becomes chloride ion. The solution of hydrogen chloride in water suffices to bring this about.

Now a phosphorus atom, instead of taking electrons from the more electropositive hydrogen to complete its group of 8, may give up its five to the more electronegative chlorine atoms, producing PCl_5, where the phosphorus has a valence of $+5$ instead of -3 as in PH_3. For similar reasons sulfur may have a valence of -2, as in H_2S, or of $+6$, as in SO_3 or SF_6. The electron theory of valence thus accounts for the fact, as seen on page 261, that the arithmetical sum of the extreme positive and negative valences of the elements does not exceed 8.

We must notice in this connection that the most strongly electropositive elements, in Group 1, are those which most

readily give up their electrons. The elements in Group 2 do so less readily, while as we approach the higher groups we find less and less tendency to lose electrons and more and more tendency to take up additional electrons, resulting in the increasing electronegative character of the elements from Group 4 to Group 7. This is of interest in connection with the chemical characteristics discussed in Chapter V, and elsewhere. It is very interesting to find that the atoms which give up electrons very readily are those which, in the solid or liquid state, readily conduct the electric current. Metallic conduction seems, in fact, to consist of a flow of electrons from atom to atom, and just as we should expect, it takes place readily in substances where the electrons are held most loosely, as in the alkali metals, and where the passage of electrons from atom to atom occurs most easily, as it does at low temperatures when the atoms are in closer contact. As a matter of fact, the conductivity of pure metals increases to infinity near the absolute zero of temperature.

In very striking accord with the above views on valence and atomic structure is the fact that during a radioactive change in which a β-particle is lost from the atomic nucleus, the result is a gain of one in positive valence, the resulting element belonging in the next higher group in the Periodic System. On the other hand the loss of an α-particle, with its two positive charges, decreases the nuclear charge by 2, and produces an element belonging two groups lower in the Periodic System, as may be seen from the table on page 279.

Moreover, the loss of a β-particle, of negligible mass, produces an element of the same atomic weight as its parent,

while the loss of an α-particle, having the mass of a helium atom, 4, produces an element four units less in atomic weight. The truth of this statement is evident if the change in atomic weight accompanying each change shown in the table on page 279 is compared with the type of rays given off during the change.

CHAPTER XVIII

DISPERSED SYSTEMS

In Chapter II a distinction was made between heterogeneous and homogeneous material, between mechanical mixtures and solutions. If we have a bottle containing water in the lower portion and moist air in the upper, we would not hesitate to call the system heterogeneous. Even if the water were blown into the air from an atomizer, we would doubtless still consider the system heterogeneous. Suppose, however, we could break up the droplets into successively smaller and smaller ones, ending finally with molecules of water vapor in air. The system finally resulting we would have to consider as homogeneous. At what stage in the disintegration process, we may well ask, did the system cease to be heterogeneous and become homogeneous? We might imagine a similar gradation starting with sand and water, which would be heterogeneous, through successively finer and finer suspensions of silica powder in water until we would have a solution of silica molecules in water. There is, evidently, no sharp boundary between systems certainly heterogeneous, on the one hand, and solutions on the other hand, and between these two extremes there are systems which should have some of the characteristics of both. These we will call **dispersed** systems, one phase being highly dispersed in another. The possible systems may be classified according to the nature of the dispersed phase and the inclosing phase as follows:

Dispersed Phase	Inclosing Phase	Type
Liquid	Gas	Fog
Gas	Liquid	Foam
Solid	Gas	Smoke
Gas	Solid	Solid foam (*e.g.*, pumice)
Liquid	Liquid	Emulsion
Solid	Liquid	Suspension
Liquid	Solid	
Solid	Solid	

The most important of these from a chemical standpoint are emulsions and suspensions, and our attention will be largely confined to them.

Brownian Movement. As the dispersed phase in suspensions and emulsions becomes more and more finely divided it is possible to get systems in which the two phases do not separate on standing under the influence of gravity. A relatively large body like a grain of sand, dropped into water, will fall through the water at a rate of speed dependent on its size, the difference in density between it and water, and the viscosity of the water. A very small sand particle will fall more slowly through the water, because as the size diminishes, the surface, upon which the resistance depends, does not decrease as fast as the weight. Fine suspensions, therefore, settle out more slowly than coarse ones. When a sufficiently minute particle is observed with a microscope it may be seen that it no longer falls in a straight line, but follows an irregular zigzag path. The reason for this is as follows: The molecules of water, according to the kinetic theory, are in rapid motion with a mean kinetic energy

proportional to the absolute temperature. Now in disordered motion of this sort some molecules, at a given instant, will be moving more rapidly and some more slowly than the average. When the particle of sand is so large compared with the water molecules that it is being bombarded by a very large number of the latter, the effect of differences in their kinetic energy will be neutralized; but when the particle gets sufficiently minute, an especially hard impact on one side of it may not be neutralized by the impacts of other molecules on the other side, hence the particle will be displaced slightly. Since these abnormally hard impacts are constantly occurring irregularly from different directions the result is the irregular zigzag movement of the particle above referred to. As smaller and smaller particles are taken, the chances for inequality in the momentum of the impacts upon them increase, and their resulting displacement also increases, for a molecule of water striking a small body will have more effect on it than upon a larger one. In fact it can be seen by the aid of the microscope that the particles of a fine suspension are in much more violent motion than those of a coarse suspension. This movement is known from its discoverer as the **Brownian movement**, and gives us very direct evidence of the truth of the kinetic theory.

When sufficiently fine particles are taken, the Brownian movement overcomes the effect of gravity so that the particles remain in permanent suspension. The system is then known as a **colloidal suspension**, or **colloidal solution**. There will be, in such a suspension, if time is allowed, an increasing concentration of particles from the upper to the lower portions of the vessel, analogous to the increasing concentration of the atmosphere from high altitudes to

lower. In fact a French physical chemist, Perrin, showed that the rate of increase in the concentration of the particles in suspensions obeys the same laws that govern the change in barometric pressure with altitude, a most striking proof of the truth of the kinetic theory and of the real existence of molecules.

The dividing line between suspensions which settle out on standing and colloidal suspensions, which remain permanently suspended, is purely one of convenience, for by applying centrifugal force it is possible to separate suspensions that would not do so under the influence of gravity alone. In general, colloidal suspensions cannot be separated by filtration through ordinary filters.

It is possible to distinguish in practice between true solutions and colloidal solutions or suspensions by reason of the great differences in their rates of diffusion. The Brownian movement of colloidal particles is so much less than the movement of the much smaller molecules of substances in true solution that the former diffuse from regions of greater to regions of smaller concentration with much less rapidity. The first distinction between the two types of solutions was made upon this basis by Graham, in 1862. He obtained the following figures for the time required for the equal diffusion of various substances:

HCl	1	$MgSO_4$	7
NaCl	2.3	Albumen	49
Sugar	7	Caramel	98

To the class of substances which diffuse slowly he gave the name **colloids**, from the Greek name for glue, a member of this class.

The molecular weight can be calculated from the rate of diffusion and also from the lowering in vapor pressure or in freezing point, as explained in Chapter IV. These methods all agree in ascribing very high molecular weights to substances in colloidal solution, as is to be expected. The following figures illustrate the values found:

Substance	Molecular Weight
Egg albumen	20,000
Gelatin	40,000
Pepsin	12,000

Optical Properties of Colloidal Suspensions. When a colloidal suspension is viewed by transmitted light it usually appears homogeneous, like a true solution, its color depending on the size of the particles and on the nature of the material. By reflected light we usually notice a somewhat different color and an opaque muddy appearance similar to that of ordinary suspensions. The microscope will detect particles as small as 0.00025 millimeter in diameter. Smaller particles than this cannot be viewed directly as they are smaller than the wave length of light, so that the latter cannot be regularly reflected from them. It is possible, however, to detect the presence of particles as small as 0.000006 millimeter by looking at them in a strong transverse beam of light against a dark background. (The diameters of the molecules of most ordinary substances are less than 0.000001 millimeter.) Although no real image of the particle may be seen, there is a scattering of the light by it so that a bright speck of light can be seen in the microscope. The same effect is responsible for the visibility of a beam of light in a dark room through illumination of dust particles invisible, perhaps, even in a microscope. A micro-

scope arranged for use with powerful transverse illumination against a dark background is called an **ultramicroscope.** By knowing the concentration of the material in a colloidal suspension, and counting the number of particles in a tiny beam of known dimensions it is possible to determine the average size of the particles.

Adsorption. Solid surfaces have the power of condensing gases upon them. The amount of gas so adsorbed depends upon the nature and area of the surface, the temperature, and the nature of the gas. The lower the temperature the more slowly do the gaseous molecules move, and the more easily are they held by the attraction exerted by the solid surface. Hence the gases which are most easily condensed to the liquid state are also more highly adsorbed by solid surfaces. Of all gases helium, which boils at 4.5° A., is least adsorbed, followed by hydrogen, whose boiling point is 20.5° A., then by gases like nitrogen, oxygen, etc., then by ammonia, water vapor, etc. It is a fact familiar to chemical analysts that considerable amounts of water may be condensed upon the surfaces of pieces of apparatus like crucibles and glass beakers, so that it is necessary to have them in a dry atmosphere in order to get exact and reproducible weights. If the solid is porous, like charcoal, or finely powdered, its surface is vastly increased, allowing the same amount to adsorb very much more of the gas. The use of charcoal to adsorb odorous gases in this way is very familiar.

A similar adsorption of dissolved substances can take place from solutions upon solid surfaces immersed in them. "Boneblack," formed by the strong heating of ground bone, turning its animal matter into charcoal, is used in the

refining of sugar to remove the yellow coloring matter present. The colored bodies are mainly substances with large molecules which are readily adsorbed on the large surface of the boneblack, from which the solution of sugar can be filtered clear and colorless. Cottonseed oil is decolorized by fuller's earth in the same way. On account of the large surface exposed by even a small amount of solid in colloidal suspension (a cube having a diameter of 1 cm. and a surface of 6 cm.^{2}, if divided into cubes with a diameter of 0.0001 cm., would have a surface of 6000 cm.^{2}) the adsorption of dissolved substances upon the colloidal particles exerts an important effect upon their properties.

Electrical Migration of Colloidal Particles. An especially important effect upon the properties of fine suspensions is exerted by adsorbed ions. It is seldom that electrolytes are absent from aqueous suspensions, and even where such is the case, the ions of water may be differentially adsorbed. Certain kinds of suspensions are prone to adsorb positive ions in excess, whereby the particles acquire a positive charge, while others, in a similar way, become negative. As a result they are able to migrate with an electric current flowing through the solution, the direction depending upon the sign of the adsorbed ions. The speed with which they move is comparable to that of the slower ions, about 7 mm. per hour under a drop of potential through the solution of 1 volt per centimeter. It is thus possible to classify suspensions as positive or negative, just as the ions themselves were classified in Chapter X. Among the positive suspensions are those of the metallic hydroxides and sulfides, the negative suspensions include arsenous sulfide, silicic acid, graphite and the noble metals.

Relation between Charge and Stability. Coagulation. Even though a suspended particle may be so small that its Brownian movement prevents its settling out under the influence of gravity, a suspension of such particles may not be stable, because of the tendency of the particles to adhere to one another on impact, forming successively larger aggregates until settling out can occur. This process may be seen when silver chloride is formed by mixing its ions. At first a very fine suspension is formed, which, if not too concentrated, appears quite stable, and may run through an ordinary filter. On standing, however, and more rapidly if the solution is heated and stirred, these extremely fine particles adhere to each other, forming eventually the familiar curdy precipitate of silver chloride. Now the effect of electrolytes upon the stability of such a suspension is very great. The presence of a charge upon the particles tends to make them repel each other and to prevent coagulation, so that a small amount of the proper electrolyte increases the stability. Suppose that we are dealing with a negative colloid like As_2S_3. If some electrolyte is added whose positive ion tends to be highly adsorbed, it may partly displace the ion giving the negative charge, leaving the particle neutral and free to coagulate with others like it. In general hydrogen and hydroxide ions are highly adsorbed, so that the addition of a small amount of acid to a suspension of arsenous sulfide suffices to coagulate it, while the addition of a small amount of alkali to a positive suspension like that of ferric hydroxide coagulates it completely. In general, then, negative suspensions are coagulated by acids and positive suspensions by alkalis. There appear to be no striking differences in the extent to which most other ions

are adsorbed, but the effect of the valence of the adsorbed ion upon its ability to coagulate a suspension is very great. Let us suppose that Na^+, Ca^{++} and Al^{+++} are adsorbed by suspended As_2S_3 to the same degree. It is evidently not the amount of substance adsorbed but the amount of positive charge that it carries with it that determines its ability to neutralize the charge on a negative suspension. To have the same amount of electricity adsorbed, we will need but half as much of the divalent Ca^{++}, and but one third as much of the trivalent Al^{+++}, as we will of the univalent Na^+. Hence it will take very much less Ca^{++} and still less Al^{+++} to have the same effect as a given amount of Na^+. Moreover, it is the amount adsorbed, and not the amount in solution, that determines the coagulating effect, and since the concentration of a substance in solution increases more rapidly than the amount adsorbed, the concentration of Na^+ in the solution must be considerably more than three times that of the Al^{+++} in order that the amount of the former adsorbed be three times the latter.

Aluminum sulfate is extensively used in connection with filtration plants to increase the efficiency of the filtration on account of the great coagulating power of aluminum ion upon the negative suspension of mud in water. The aluminum hydroxide formed by the hydrolysis of the aluminum sulfate is itself a positive colloid, and also aids considerably in the coagulation, since a positive colloid acts like a positive ion in neutralizing the charge on a negative suspension.

The ions in sea water have a similar coagulating effect upon muddy river water discharged into it, a factor which aids in the formation of bars at river mouths.

Most dyes are very fine suspensions, which are themselves

adsorbed or absorbed in animal or vegetable fibers. When the fiber is unable to hold the dye permanently, the color may frequently be made "fast" by using a coagulant, called a "mordant." The mordant is the salt of a polyvalent ion like Al^{+++} or Sn^{++++}, which can diffuse into the fiber and hydrolyze, giving a positive hydroxide, which can hold the dye firmly. A "lake" is a pigment made of such a coagulum of a hydroxide, like $Al(OH)_3$, with a suitable dye. The famous "purple of Cassius" is a similar coagulum of gold and stannic hydroxide, formed simultaneously in the reaction of stannous ion with chlor-aurate ion, as follows:

$$2\,AuCl_4^- + 3\,Sn^{++} + 12\,H_2O = 2\,Au + 3\,Sn(OH)_4 + 12\,H^+ + 8\,Cl^-.$$

In washing precipitates it is often found that the precipitate tends to become suspended and run through the filter. It is possible to prevent this re-suspension by washing with water containing a little acid, or ammonium salt, or ammonia, etc., as the case requires.

The effect of the valence of negative ions in coagulating positive suspensions follows the principles laid down for the corresponding effect upon negative colloids. Ferric hydroxide suspension, for example, is more easily coagulated by sodium sulfate than by sodium chloride.

Emulsions. We have thus far been considering dispersed systems in which a solid is suspended in a liquid. We will now consider those systems, called **emulsions**, in which the suspended phase is a liquid. Much of what has been said in regard to solid suspensions applies here. When the suspended droplets are small enough, as in cream, they are subject to Brownian movement, though in this case not sufficient to prevent their slow rise to the top by reason of gravity.

The optical properties of emulsions are similar to those of suspensions. It is possible, however, to have stable emulsions with the suspended material less highly dispersed and in larger amounts than is the case ordinarily with solid suspensions, as illustrated by cream and mayonnaise dressing. In order to do this, however, an emulsifying agent must be used, for two pure liquids will not form a stable emulsion. The reason for this is as follows:

Whenever it is possible for two suspended droplets to come together they will coalesce into one, for the surface tension operates to make the surface as small as possible, and one spherical drop will have less surface than two of the same total volume. In order to prevent their coalescing it is desirable to have the liquid in which they are suspended viscous, but especially is it necessary that the film of liquid which separates them when they are close together should be difficult to rupture, like the soap film which prevents two adjacent air bubbles from coalescing. Now a stable liquid film can be produced by some substance which greatly lowers the surface tension of the liquid. An exact proof of this could be given, but the following simpler explanation may suffice. The diminution in the surface tension is an evidence that the substance added diminishes the attractive forces of the molecules within the liquid, consequently there will be a tendency for molecules of the solvent to restore the condition of the pure solvent, where the molecules are probably closer together, by squeezing out, as it were, the molecules of the solute, which will therefore tend to be concentrated at the surface, still farther lowering the surface tension. In fact we find that the surface tension of soap solutions is much less than that of water, and also that the

tension at a surface that has stood for a short time is less than it is at a fresh surface, as illustrated by the following figures:

	Surface Tension	
	Fresh Surface	Old Surface
Water	79	79
1.25 per cent soap solution,	62	26

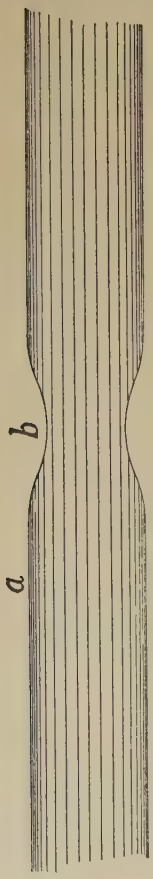


Fig. 14.—Behavior of Soap Film.

Suppose, now, that we consider a film of such a solution, representing in Fig. 14 at *a* the greater concentration of the soap at the surface by the shading. If a strain is put upon the film so that it starts to rupture at a certain place, represented at *b*, the effect is to bring fresh solution from the interior to the surface at this point, solution in which the soap is at first less concentrated, and whose surface tension is, therefore, greater than that of the old surface. Consequently, whenever rupture threatens, the film becomes automatically stronger, and hence it is stable. Sufficient soap dissolved in water will therefore give either a stable foam, if shaken with air, or a stable emulsion if shaken with oil. Other substances like saponin, gelatin, albumen, the casein of milk, etc., may have the same effect in greater or less degree. The substances in the egg act in this way in making mayonnaise. Milk, when concentrated in the form of evaporated milk, can serve also for making mayonnaise.

It is possible to have either phase the inclosed phase, the oil being the inclosing phase in mayonnaise that has "separated," and in the water-petroleum emulsions that often give trouble in oil wells. In this case the crude oil is the solution, and hence can give stable films separating the water drops. An emulsion of water in benzene can be made by dissolving in the latter a magnesium soap, which lowers its surface tension. There is a tendency, also, for the phase present in smallest amount to be the inclosed phase, and one of the secrets of success in making mayonnaise is accordingly to wet the sides of the vessel with egg, and to add the oil slowly at first.

Jellies. When the inclosed phase of an emulsion is present in sufficient amount, the droplets begin to press on each other, interfering with their spherical tendency and substituting a structure which would appear, in cross section, somewhat like a honeycomb. The droplets can no longer slide over each other rapidly, and any stress tending to deform the mass results in deforming the droplets, increasing their surface. On the removal of the stress their surface tension operates to restore their symmetry. Consequently such an emulsion is elastic, and represents one type of jelly.

Emulsion Colloids. Allied in many respects to emulsions are solutions of many substances produced by animal and vegetable life, including glue, gelatin, albumens, tannin, gums and starch. Their properties may be deduced, to a considerable extent, from the supposition that they are highly dispersed emulsions. The two phases, unlike the familiar oil-water emulsions, are soluble in each other to a considerable extent, so that the surface tension between

them is very slight. On this account there is little adsorption of ions at their bounding surfaces, and their stability is little affected by ionic charges. This distribution of water between the two phases may, however, be considerably changed by the addition of electrolytes, even to the extent of "salting out" the colloid, as is done in making soap, when common salt is used to make the soap separate from the solution. The effectiveness of various electrolytes in salting out colloids follows roughly the order in which they affect the surface tension of water. The effectiveness of various anions decreases in the following order: citrate, sulfate, acetate, chloride, nitrate, iodide, sulfocyanate, so that sodium sulfate, for example, would be far more effective than sodium nitrate in salting out a colloid.

On account of the ease with which most colloids of this type remain in solution in large concentrations in water, they are often called **hydrophilic** colloids, those which "like water," as distinguished from the relatively unstable **hydrophobic** colloids, those which "hate water," which we considered earlier.

Just as a fine emulsion is viscous, if at all concentrated, so these emulsion colloids, or hydrophilic colloids, are often very viscous, as illustrated by solutions of glue or gelatin. Furthermore, when an emulsion contains enough of the inclosed phase so that the droplets deform each other, we begin to get the properties of a jelly. Similarly, by lowering the temperature, or on evaporation of water, the two phases apparently present in solutions of emulsion colloids usually become of such relative amounts as to produce gelatinization. The swelling or shrinking of these jellies when placed in solutions of different electrolytes plays an important

part in biological processes, since much of the material of the living organism is colloidal in nature.

As one phase of an emulsion becomes more viscous it approaches a solid in properties, hence there is no sharp distinction between a solid suspension and an emulsion. The corresponding jelly, moreover, may be less like the jelly of a true emulsion, like stiff mayonnaise, and more like a wet sponge, where we have a liquid dispersed within an elastic fibrous solid. Silicic acid jelly seems to be of this nature.

Protective Colloids. If an oil emulsion were mixed with a metallic suspension, the oil drops would tend to inclose the metal particles, and the resulting system would behave essentially like a pure emulsion. Similarly, when an emulsion colloid, or hydrophilic colloid, is mixed with a hydrophobic colloid, the mixture behaves like a colloid of the former class. Since the hydrophilic colloids are relatively stable, a hydrophobic colloid may be made stable in this way. For example, if gelatin is present in a solution in which silver chloride is formed from its ions, each particle of the silver chloride is coated with gelatin so as to prevent the coagulation that would otherwise ensue. The retention of this highly dispersed state in the solidified gelatin makes possible the photographic dry plate. Again, when gelatin is added to a suspension of arsenous sulfide it requires much more concentrated acid to coagulate it.

Preparation of Colloidal Solutions. In addition to the colloids obtained from biological sources, like gelatin, albumens, starches, etc., it is possible to prepare highly dispersed systems of other materials by various methods which may be classified as dispersion or condensation methods,

according, respectively, as we start with undispersed material or with molecularly dispersed material, molecules and ions.

(*a*) **Dispersion Methods.** Colloidal solutions of the nobler metals may be prepared by passing an arc between electrodes of that metal under water. The metal is vaporized in the arc and the vapor is condensed to solid particles in a highly dispersed state.

Previously coagulated material may often be redispersed by washing out the coagulant, as occurs in washing certain precipitates. Basic ferric acetate, precipitated by boiling a solution containing ferric acetate, may be redispersed by washing with water containing a trace of acid.

Some substances can be dispersed by the aid of a "**peptonizer**," usually a protective colloid, taking its name from the action of pepsin in digestion in dispersing albuminous material in the process of digestion. Thus graphite can be peptonized, or suspended, by grinding it with tannin. The resulting solution is known commercially as "aquadag," and can be used as a lubricant. The cleansing action of soap, which is in the colloidal state when dissolved in water (not when in alcohol), is of this nature.

(*b*) **Condensation Methods.** By starting with ordinary solutions it is possible to get suspensions by suitable means. Thus a solution of a ferric chloride always contains free H^+, Cl^- and $Fe(OH)_3$ (or basic chloride), the last of which is partly agglomerated, so that it will not pass through a very fine membrane like parchment. Accordingly, if such a solution is separated by parchment from pure water, the H^+ and Cl^- can diffuse out. The $Fe(OH)_3$ accumulates as the hydrolysis proceeds, as represented by the equation,

$$Fe^{+++} + 3\,Cl^- + 3\,H_2O = Fe(OH)_3 + 3\,H^+ + 3\,Cl^-.$$

By continually renewing the water into which the hydrochloric acid diffuses, the hydrolysis may be made complete, leaving a colloidal solution of ferric hydroxide. Such a process of separation by differential diffusion is called dialysis. Other hydroxides can be obtained in colloidal solution by the same method. That a colloidal solution is obtained by dialysis but not by the addition of alkali, is due to the coagulating effect of the larger amount of electrolyte, consisting of chloride ions and especially hydroxide ions which would be present under the latter circumstances.

Whenever a relatively insoluble substance can be produced in the absence of any considerable amount of electrolytes, it is possible to prepare it as a colloid. Thus the action of H_2S on a solution of As_2O_3 will give a suspension of As_2S_3, since the substances involved are all practically un-ionized. A suspension of HgS can be obtained by the action of H_2S on $Hg(CN)_2$ for the same reason. Colloidal gold can be prepared by the reduction of a very dilute solution of $HAuCl_4$ by some non-ionized reducing agent, such as formaldehyde, CH_2O, or a solution of phosphorus in ether. The addition of some protective colloid, like gelatin, allows the solution of the metal to be prepared in much more stable form, and also more concentrated. The "argyrol," used in curing cold in the head, is a concentrated protected solution of colloidal silver.

EXERCISES

1. Discuss the conditions necessary for the existence of stable foams and emulsions.

2. Summarize the characteristics of hydrophilic and hydrophobic colloids, respectively.

3. Assuming that you have discovered that a certain colloid migrates with the positive current, decide whether it would be coagulated more easily by HCl or NaOH.

4. When a substance is dispersed in a liquid the behavior of the system will depend mainly upon the following factors: (*a*) the size of the dispersed particles, (*b*) the magnitude of the surface tension between the phases, (*c*) whether the dispersed phase is solid or liquid, (*d*) whether the dispersed particles adsorb positive or negative ions more readily. Decide what effect, if any, each of the above factors would have upon each of the following phenomena: (1) the Brownian movement, (2) the electric migration, (3) the rate of diffusion, (4) coagulation, (5) separation on standing, (6) adsorbing power, (7) protective action on other dispersed substances.

5. What conditions should be observed in the formation of colloidal solutions?

6. Outline experiments to enable you to determine the most effective means for coagulating a colloidal suspension of an unfamiliar substance.

7. Make a classification of dispersed systems that will, in your opinion, best express their various behaviors.

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